

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:
SAINI ET AL.

Serial No.: **10/736,339**

Filed: **DECEMBER 15, 2003**

Title: **“ON-THE FLY COATING OF ACID-
RELEASING DEGRADABLE MATERIAL
ONTO A PARTICULATE”**

§ Group Art Unit: **1792**

§ Confirmation No.: **3700**

§ Examiner: **LIGHTFOOT, ELENA TSOY**

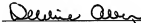
§ Atty. Docket No: **2001-IP-005484U1P1**

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APPELLANTS' BRIEF (37 C.F.R. § 41.37)

This Brief is submitted in support of Appellants' Notice of Appeal from the rejections in the Final Office Action dated April 6, 2009 (the "Final Office Action"), and the Advisory Action dated July 6, 2009 (the "Advisory Action"). This Appeal Brief is being submitted with a request for a one-month extension of time extending the period for filing to November 5, 2009. Therefore, this Appeal Brief is timely filed.

I. IDENTIFICATION OF THE REAL PARTY OF INTEREST

The real party in interest is:

Halliburton Energy Services, Inc.
10200 Bellaire Blvd.
Houston, Texas 77072

by virtue of assignments by the inventors as duly recorded in the Assignment Branch of the U.S. Patent and Trademark Office.

II. IDENTIFICATION OF RELATED APPEALS AND INTERFERENCES

There are no related appeals or interferences, to Appellants' knowledge.

III. STATUS OF THE CLAIMS

The application as originally filed contained 41 claims. Claims 42-61 are pending.

The Examiner has rejected claims 42-48 under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent No. 6,209,643 issued to Nguyen *et al.* (hereinafter "*Nguyen*") in view of U.S. Patent No. 6,458,867 issued to Wang *et al.* (hereinafter "*Wang*") in further view of U.S. Patent No. 6,817,414 issued to Lee *et al.* (hereinafter "*Lee*").¹

The Examiner also has rejected claims 42-48 under 35 U.S.C. § 103(a) as being unpatentable over *Nguyen* in view of *Wang*, and U.S. Patent No. 5,192,615 issued to McDougall *et al.* (hereinafter "*McDougall*"), or over *Nguyen* in view of *Wang* in further view of *Lee* in further view of *McDougall*.²

The Examiner also has rejected claims 55-61 under 35 U.S.C. § 103(a) as being unpatentable over *Nguyen* in view of *Wang* and *McDougall*, or over *Nguyen* in view of *Wang* in further view of *Lee* in further view of *McDougall*.

The Examiner also has rejected claims 49-54 under 35 U.S.C. § 103(a) as being unpatentable over *Nguyen* in view of *Wang*, *Lee*, and U.S. Patent No. 6,669,771 to Tokiwa *et al.* (hereinafter "*Tokiwa*").³

Finally, the Examiner has also provisionally rejected claims 42-54 under the judicially created doctrine of obviousness-type double patenting as being unpatentable over claims 1-7, 9-11, and 13-17 of co-pending U.S. Application Serial No. 11/046,043 in view of U.S. Patent No. 4,829,100.

¹ Copies of *Nguyen*, *Wang*, and *Lee* are provided in Appendix E to this Brief.

² A copy of *McDougall* is provided in Appendix E to this Brief.

³ A copy of *Tokiwa* is provided in Appendix E to this Brief.

Appellants herein appeal the above rejections of claims 42-61 under 35 U.S.C. § 103(a) as improper. A listing of all appealed claims is provided in Appendix A in this Brief.

IV. STATUS OF ANY AMENDMENT FILED SUBSEQUENT TO FINAL REJECTION

No amendment has been filed subsequent to final rejection.

V. SUMMARY OF THE CLAIMED SUBJECT MATTER

With regard to the independent claims currently under Appeal, Appellants provide the following concise explanation of the subject matter recited in the claim elements. For brevity, Appellants do not necessarily identify every portion of the Specification and drawings relevant to the recited claim elements. Additionally, this explanation should not be used to limit Appellants' claims but is intended to assist the Board in considering the Appeal of this Application.

Appellants' invention relates to fluids and compositions for treating subterranean formations. (*See* Specification at page 5, lines 1-2.)⁴ More particularly, Appellants' invention relates to improved methods and compositions for degrading filter cake deposited in a subterranean formation. (*See id.* at page 5, lines 2-3.)

Certain embodiments of Appellants' invention provide methods of degrading filter cake in a subterranean formation that comprise the following steps: combining an acid-releasing degradable material with a solvent or a plasticizer to create a coating solution, wherein the acid-releasing degradable material comprises at least one acid-releasing degradable material selected from the group consisting of: poly(orthoester); a lactide, a poly(lactide); a glycolide; a poly(glycolide); a poly(ϵ -caprolactone); a poly(hydroxybutyrate); a substantially water insoluble anhydride; a poly(anhydride); a poly(amino acid); a mixture of one of the above-listed compounds; a copolymer of two or more of the above-listed compounds; and any combination thereof; coating the coating solution onto a particulate on-the-fly to create coated particulates; placing the coated particulates into a subterranean formation so that at least a portion of the coated particulates become incorporated in a pack substantially adjacent to a filter cake; allowing the acid-releasing degradable material to produce acid; and allowing the acid to contact and degrade a portion of the filter cake. (*See, e.g., id.* at page 4, lines 9-15; *id.* at page 5, lines 4-11; *id.* at page 6, lines 15-29; claim 42.)

⁴ A copy of the specification as filed is provided in Appendix D to this Brief.

Other embodiments of Appellants' invention provide methods of using a portion of a gravel pack to degrade a portion of a filter cake that comprise the following steps: combining an acid-releasing degradable material with a solvent or a plasticizer to create a coating solution; wherein the acid-releasing degradable material comprises at least one acid-releasing degradable material selected from the group consisting of: poly(orthoester); a poly(ϵ -caprolactone); a poly(hydroxybutyrate); a substantially water insoluble anhydride; a poly(anhydride); a poly(amino acid); a mixture of one of the above-listed compounds; a copolymer of two or more of the above-listed compounds; and any combination thereof; coating the coating solution onto gravel on-the-fly to create coated gravel; introducing the coated gravel to a well bore having a filter cake so that at least a portion of the coated gravel is incorporated in a gravel pack substantially adjacent to the filter cake; allowing the acid-releasing degradable material to produce acid; and, allowing the acid to contact and degrade a portion of the filter cake. (See, e.g., *id.* at page 4, lines 9-15; *id.* at page 5, lines 4-11; *id.* at page 6, lines 15-29; *id.* at page 8, line 25 - page 9, line 3; claim 49.)

Other embodiments of Appellants' invention provide methods of degrading filter cake in a subterranean formation comprising the following steps: combining an acid-releasing degradable material with a plasticizer to create a coating solution, with the proviso that the plasticizer does not comprise a starch; coating the coating solution onto a particulate on-the-fly to create coated particulates; placing the coated particulates into a subterranean formation so that at least a portion of the coated particulates become incorporated in a pack substantially adjacent to a filter cake; allowing the acid-releasing degradable material to produce acid; and allowing the acid to contact and degrade a portion of the filter cake. (See, e.g., *id.* at page 4, lines 9-15; *id.* at page 5, lines 4-11; *id.* at page 6, lines 3-29; claim 55.)

VI. GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

The Examiner has rejected claims 42-48 under 35 U.S.C. § 103(a) as being unpatentable over *Nguyen* in view of *Wang* and *Lee*.

The Examiner also has rejected claims 42-48 under 35 U.S.C. § 103(a) as being unpatentable over *Nguyen* in view of *Wang* and *McDougall*, or over *Nguyen* in view of *Wang* in further view of *Lee* in further view of *McDougall*.

The Examiner also has rejected claims 55-61 under 35 U.S.C. § 103(a) as being unpatentable over *Nguyen* in view of *Wang* and *McDougall*, or over *Nguyen* in view of *Wang* in further view of *Lee* in further view of *McDougall*.

Finally, the Examiner has rejected claims 49-54 under 35 U.S.C. § 103(a) as being unpatentable over *Nguyen* in view of *Wang*, *Lee*, and *Tokiwa*.

VII. ARGUMENTS

In order for a reference or combination of references to form the basis for a rejection under § 103(a), a *prima facie* case of obviousness must be established. MANUAL OF PATENT EXAMINING PROCEDURE (“MPEP”) § 2142 (2008). Obviousness is determined by construing the scope of the prior art, identifying the differences between the claims and the prior art, determining the level of skill in the pertinent art at the time of the invention, and considering objective evidence present in the application indicating obviousness or nonobviousness. *Id.* at § 2141; *Graham v. John Deere*, 383 U.S. 1, 17 (1966). Moreover, there must be some articulated reasoning with some rational underpinning to support the alleged obviousness of the proposed modifications or combinations of prior art. MPEP at § 2143.01; *KSR International Co. v. Teleflex, Inc.*, 550 U.S. 398, 127 S.Ct. 1727, 1731 (2007); *In re Kahn*, 441 F.3d 977, 988, 78 USPQ2d 1329, 1336 (Fed. Cir. 2006). For at least the reasons provided below, Appellants submit that the Examiner has not established the required elements of a *prima facie* case of obviousness, nor can the cited references provide such a *prima facie* case.

A. The cited prior art cannot obviate Appellants’ claims because *Nguyen* does not teach or suggest an acid-releasing degradable material.

Nguyen does not discuss any material as being “degradable” or describe any material degrading to produce an acid in the methods disclosed therein. The Examiner does not dispute these facts. Instead, the Examiner asserts – without citation to any reference or technical analysis – that the tackifying compounds coated onto particulates in *Nguyen* “should be” an “acid-releasing degradable material” since *Nguyen* “teaches that coated treatment chemical is subsequently released within the subterranean formation.” Based on this assertion, the Examiner concludes that a degradable tackifying compound “may be used” in *Nguyen*. (See Final Office Action at 6; Advisory Action at 2-3.) Respectfully, *Nguyen* does not support these assertions.

The tackifying compositions disclosed in *Nguyen* are not “degradable.” The tackifying compositions of *Nguyen* are used to adhere the coated particulates to one another in order to uniformly disperse a treatment chemical in a particulate pack and prevent particulate

migration and flowback. (*Nguyen* at col. 3, ll. 49-58 & col. 4, ll. 57-59.) The tackifying compositions would not be able to perform these functions if they degrade once downhole as the Examiner suggests. Nor does *Nguyen*'s inclusion of certain compounds of the same chemical family (e.g., polyamides) as certain acid-releasing degradable materials make the tackifying compositions of *Nguyen* "degradable". Similarly, the mechanism for release of treatment chemicals has nothing to do with the degradability of the tackifying compositions. *Nguyen* notes that release of treatment chemical is accomplished as "[t]he tackifying compound changes the interfacial surface tension effects of fluids in contact with the treatment chemicals to reduce wetting of the treatment chemicals by the formation fluids thereby reducing the dissolution rate of the chemicals." (*Nguyen* at col. 4, ll. 51-56 (emphasis added).) This process does not state or imply that the tackifying compositions "should be degradable," and in fact has nothing to do with the degradability of the tackifying compositions at all.

The Examiner cites a passage of *Nguyen* that uses the word "any" in describing the tackifying compositions that may be used, asserting that *Nguyen*'s teaching of "any" tackifying compositions "does not limit [Nguyen's] teaching to particular tackifying compounds and thus *Nguyen* "teaches implicitly" that an "acid-releasing degradable tackifying composition" may be used. (Advisory Action at 2-3; Final Office Action at 7.) However, even if the tackifying compounds usable in *Nguyen* "may" be degradable or acid-releasing materials (as discussed above, they are not), such a possibility "is not sufficient to establish the inherency of that characteristic." See MPEP at § 2112. The Manual of Patent Examining Procedure instead requires "a basis in fact and/or technical reasoning ... that the allegedly inherent characteristic necessarily flows from the teachings of the applied prior art." *Id.* (emphasis in original). The relevant passage of *Nguyen* reads as follows:

Compounds suitable for use as a tackifying compound comprise substantially any compound which when in liquid form or in a solvent solution will form a non-hardening coating, by themselves....

(*Nguyen* at col. 5, ll. 10-13 (emphasis added).) Neither this passage nor anything else in *Nguyen* suggests that its tackifying compositions are necessarily degradable, or that "acid-releasing degradable tackifying compositions" actually exist. Nor does the Examiner point to any substance disclosed in *Nguyen* or elsewhere in the prior art that may constitute such an "acid-releasing degradable tackifying composition" (i.e., a composition that in liquid form or in a

solvent solution will form a non-hardening coating, by itself and would degrade to produce an acid). Indeed, as discussed below, the polyglycolic acids disclosed in *Lee* are not tackifying compositions at all (*i.e.*, they do not form a non-hardening coating), and thus could not constitute “acid-releasing degradable tackifying compositions” that the Examiner believes *Nguyen* to “implicitly” teach.

B. The cited prior art cannot obviate Appellants’ claims because the degradable materials disclosed in *Lee* and *Wang* cannot be combined with or used as substitutes for the tackifying compounds of *Nguyen*.

Acknowledging that *Nguyen* does not disclose any of the specific acid-releasing degradable materials listed in claims 42 and 49, the Examiner asserts that selecting one of the materials disclosed in *Lee* for use as a tackifying composition in *Nguyen* would be obvious since “selection of a known material base on its suitability for its intended use” supports a *prima facie* case of obviousness. (Advisory Action at 3.) As demonstrated in the above-quoted passage from *Nguyen*, *Nguyen* explicitly limits the tackifying compositions to compounds that “when in liquid form or in a solvent solution will form a non-hardening coating, by themselves...” (*Id.* at col. 5, ll. 10-13.) Nothing in *Lee* indicates that the lactic polymers disclosed therein meet these requirements. The “intended use” of the tackifying compositions of *Nguyen* is to adhere the coated particulates to one another in order to uniformly disperse a treatment chemical in a particulate pack and prevent particulate migration and flowback. *Nguyen* also states, as noted above, that the tackifying compound may be used to “change[] the interfacial surface tension effects of fluids in contact with the treatment chemicals to reduce wetting of the treatment chemicals by the formation fluids thereby reducing the dissolution rate of the chemicals.” There is no indication that the lactic polymers disclosed in *Lee* would be suitable for (or even capable of performing) the intended uses of the tackifying compositions in *Nguyen*.

Instead of addressing the explicit intended uses in *Nguyen*, the Examiner references the suitability of the polymers in *Lee* for hydrolyzing to produce an acid, as taught in *Wang*. However, the Examiner cites to nothing indicating that a person of skill in the art would select a material for a tackifying composition in *Nguyen* based on its ability to hydrolyze to produce an acid. *Wang* deals with the unrelated art of lubricant coatings for medical devices (*see Wang* at Abstract), and the Examiner provides no explanation for why a person of skill in the art to which the present invention (or *Nguyen* and *Lee*) pertains would consider such unrelated teachings in selecting a suitable tackifying compound. Rather, the Examiner cobbles together

the unrelated teachings of *Nguyen*, *Lee*, and *Wang* simply because the categories of possible “acid-releasing degradable materials” in Appellants’ specification overlap with the categories of compounds in *Nguyen* and *Lee*. Such a combination constitutes an impermissible use of hindsight that cannot form a basis for a proper § 103 rejection. MPEP at § 2142.

C. The cited prior art cannot obviate Appellants’ claims because neither *Nguyen* nor any obvious modification of *Nguyen* performs the step of “allowing the acid-releasing degradable material to produce acid”.

Each of the rejected claims recites a method that includes the step of “allowing the acid-releasing degradable material to produce acid.” As noted above, the Examiner cites nothing in *Nguyen* that describes a degradable material (or any other material, for that matter) producing an acid. The Examiner relies on *Wang* for the notion that “it is a common knowledge in the art” that the polyesters and polyamides “hydrolyze either through acid or base catalysis, to a carboxylic acid.” (Final Office Action at 4; *see also* Non-Final Office Action dated November 14, 2008.) However, as Appellants argued in their prior responses, in order to teach or suggest the claimed method step of “allowing the acid-releasing degradable material to produce an acid,” it is not enough for the prior art to teach a compound that is merely capable of performing this step. Rather, the method step itself must be obvious to perform in *Nguyen*. *Nguyen* describes no method or process in which the tackifying compositions disclosed therein undergo “acid-base catalysis” reactions described in *Wang*, and the Examiner provides no explanation for why these reactions must necessarily occur in *Nguyen*. Even if “it is a common knowledge in the art” that polyesters, polyamides, or any of the materials described in *Nguyen* or *Lee* undergo such hydrolysis – and as discussed in Section A. above, the materials in *Nguyen* are not necessarily capable of doing so – there is no reason that a person of skill in the art would modify the methods of *Nguyen* to include this hydrolysis. MPEP at § 2143.01 (fact that all elements are “known” and “can be combined” is not sufficient; must be some rationale for combining them).

Moreover, as discussed in Sections A. and B. above, the tackifying composition disclosed in *Nguyen* is used to uniformly disperse a treatment chemical in a particulate pack, prevent particulate migration and flowback, and/or “change[] the interfacial surface tension effects of fluids in contact with the treatment chemicals to reduce wetting of the treatment chemicals by the formation fluids thereby reducing the dissolution rate of the chemicals.” (*Nguyen* at col. 3, ll. 49-58 & col. 4, ll. 52-55.) If the tackifying composition of *Nguyen* degrades to produce an acid, it would not perform these functions, rendering the tackifying

compositions unsatisfactory for their stated purpose. Such a modification of *Nguyen* cannot render Appellants' invention obvious. See MPEP at § 2143.01 (V).

In her most recent Advisory Action, the Examiner provides no response to these arguments made previously in Appellants' response to the Final Office Action. Instead, the Examiner simply notes that "one of ordinary skill would have a reasonable expectation of success of using polylactide of Lee because Nguyen does not limit their teaching to particular tackifying compounds...." (Advisory Action at 3.) However, this assertion of a "reasonable expectation of success" does not address the deficiency discussed above – the lack of any reason why a person of skill in the art would modify the methods disclosed in *Nguyen* to "allow[] the acid-releasing degradable material to produce acid." Even if such a modification would be "successful" (for some purpose that the Examiner does not specify), without some "articulated reasoning with some rational underpinning" for making the modification, all of the rejections of Appellants' claims are improper. See MPEP at § 2143.01; *KSR International Co. v. Teleflex, Inc.*, 550 U.S. 398, 127 S.Ct. 1727, 1731 (2007); *In re Kahn*, 441 F.3d 977, 988, 78 USPQ2d 1329, 1336 (Fed. Cir. 2006).

D. The Examiner's combinations of *Nguyen* and *Lee* cannot be obvious because they are incompatible with and teaches away from coating a coating solution onto a particulate "on-the-fly".

Each of the rejected claims also recites a method that includes the step of "coating the coating solution onto a particulate on-the-fly" to create coated particulates or gravel. However, the acid-releasing degradable materials as disclosed in *Lee* cannot be used to coat a particulate or gravel "on-the-fly". As Appellants have argued previously, the specification of the present application defines that the "on-the-fly" step in the present invention means that the particulates and coating solution "are combined and mixed while continuing to flow as a single stream as a part of the on-going treatment at the job site." (Specification at ¶ 0025.) However, *Lee* teaches that the polyglycolic acid must be heated to at least 210°F and maintained at that temperature to remain in liquid form. (*Lee* at col. 3, l. 64 - col. 4, l. 11.) Gravel particles are then "slowly added and constantly stirred" into the liquid polyglycolic acid, cooled to room temperature, and ground "using a mortar and pestle or other grinding device, and sieved through a screen ... to remove fine particles." (*Id.*) A person of ordinary skill in the art would not expect that these teachings of heating, cooling, and sizing the materials prior to use – which *Lee* does not describe as optional, and must be considered in determining whether *Lee* obviates

Appellants' claims – could be combined with a method that involves coating a particulate “on-the-fly.” See MPEP at § 2141.02 (“A prior art reference must be considered in its entirety, *i.e.*, as a whole, including portions that would lead away from the claimed invention.”). Such a complicated method teaches away from and discourages a person of skill in the art from using the degradable materials described in *Lee* in an “on-the-fly” coating step. *Id.* at § 2145 (X.D.) In view of the markedly-different and complicated coating process taught in *Lee*, coating the degradable materials of *Lee* onto a particulate “on-the-fly,” as Appellants' claims require, would not be obvious.

In her most recent Advisory Action, the Examiner provides no response to these arguments made previously in Appellants' response to the Final Office Action. Without addressing this incompatibility of the combined prior art, the rejections of Appellants' claims in view of *Lee* are improper.

E. The combination of *Nguyen*, *Wang*, *Lee*, and *McDougall* cannot obviate claims 55-61 because that combination does not teach a plasticizer that does not comprise starch.

The Examiner explicitly acknowledges that “[t]he cited prior art fails to teach ... a plasticizer other than starch.” (Final Office Action at 3.) Instead, the Examiner asserts that it would be obvious to add “other additives commonly used in hydraulic fracturing fluids” listed in *McDougall* to the fluid suspension of *Nguyen* “with the expectation of providing the desired control of fluid loss.” (*Id.* at 3-4.) However, the Examiner fails to establish that any of these substances are plasticizers, and *McDougall* certainly does not describe them as such. Even if any of the other additives listed in *McDougall* were plasticizers, it would not be obvious to combine them with the methods and compositions of *Nguyen* and *Lee*. *McDougall* notes that such additives are commonly used in fracturing fluids as “wall-building” (*i.e.*, filter cake creating) agents (col. 8, ll. 7-10), whereas *Lee* and Applicants' claims are directed to methods of degrading a portion of a filter cake. Persons skilled in the art would not think it obvious to combine additives that are used for such different and conflicting purposes.

In her most recent Advisory Action, the Examiner provides no response to these arguments made previously in Appellants' response to the Final Office Action. Without addressing this incompatibility of the combined prior art, the rejections of Appellants' claims 55-61 are improper.

F. Appellants will hold in abeyance their response to the provisional double-patenting rejections of claims 42-54.

Claims 42-54 stand provisionally rejected under the judicially created doctrine of obviousness-type double patenting as being unpatentable over claims 1-7, 9-11, and 13-17 of co-pending U.S. Application Serial No. 11/046,043 in view of U.S. Patent No. 4,829,100. As this rejection is provisional in nature, Appellants are not required to respond to this rejection until allowable subject matter is indicated in U.S. Application Serial No. 11/046,043, and thus Appellants will hold in abeyance their response until allowable subject matter is indicated. MPEP at § 804. If the double-patenting rejection remains pending in the present application and is no longer provisional, Applicants will consider filing a terminal disclaimer at that time.

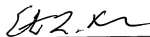
VIII. SUMMARY

In light of the foregoing, Appellants respectfully request that the final rejections of the pending claims should be reversed and the application be remanded for allowance of the pending claims, or, alternatively, remand the application for further examination if appropriate references can be found by the Examiner.

Appellants hereby petition under the provisions of 37 C.F.R. § 1.136(a) for a one-month extension of time to file this Brief, extending the deadline for filing this brief from October 5, 2009 to November 5, 2009.

The Commissioner is hereby authorized to debit Baker Botts L.L.P.'s Deposit Account No. 02-0383, Order Number 063718.1357, in the amount of \$670.00 for (1) the fee of \$130.00 under 37 C.F.R. § 1.17(a)(1) for the One-Month Petition for Extension of Time to File this Brief, and (2) the fee of \$540.00 under 37 C.F.R. § 41.20(b)(2) for filing an appeal brief. Should the Commissioner deem that any additional fees are due, including any fees for extensions of time, the Commissioner is authorized to debit Baker Botts L.L.P.'s Deposit Account No. 02-0383, Order Number 063718.1357.

Respectfully submitted,



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Date: November 5, 2009

APPENDIX A: CLAIMS INVOLVED IN APPEAL

1. - 41. (Cancelled)

42. (Previously Presented) A method of degrading filter cake in a subterranean formation comprising the steps of:

combining an acid-releasing degradable material with a solvent or a plasticizer to create a coating solution, wherein the acid-releasing degradable material comprises at least one acid-releasing degradable material selected from the group consisting of: poly(orthoester); a lactide, a poly(lactide); a glycolide; a poly(glycolide); a poly(ϵ -caprolactone); a poly(hydroxybutyrate); a substantially water insoluble anhydride; a poly(anhydride); a poly(amino acid); a mixture of one of the above-listed compounds; a copolymer of two or more of the above-listed compounds; and any combination thereof;

coating the coating solution onto a particulate on-the-fly to create coated particulates;

placing the coated particulates into a subterranean formation so that at least a portion of the coated particulates become incorporated in a pack substantially adjacent to a filter cake;

allowing the acid-releasing degradable material to produce acid; and

allowing the acid to contact and degrade a portion of the filter cake.

43. (Previously Presented) The method of claim 42 wherein the filter cake comprises a filter cake on the walls of a well bore or a filter cake on the walls of a fracture.

44. (Previously Presented) The method of claim 42 wherein the particulates are coated with from about 0.1% to about 20% acid-releasing degradable material by weight of the particulates.

45. (Previously Presented) The method of claim 42 wherein acid-releasing degradable material comprises a material that is substantially water insoluble and that degrades over time in an aqueous environment.

46. (Previously Presented) The method of claim 42 wherein the solvent comprises at least one solvent selected from the group consisting of: acetone; propylene carbonate; di(propylene glycol) methyl ether; di(propylene glycol) propyl ether; di(propylene glycol) butyl ether; di(propylene glycol) methyl ether acetate; isopropyl alcohol; chloroform; dichloromethane; trichloromethane; 1,2-dichlorobenzene; tetrahydrofuran; benzene; acetonitrile;

dioxane; dimethylformamide; toluene; ethyl acetate; isoamyl alcohol; N-methylpyrrolidone; xylene; dichloroacetic acid; m-cresol; hexafluoroisopropanol; diphenyl ether; acetonitrile; methanol; ethyl benzene; naphthalene; naphtha; and any combination thereof.

47. (Previously Presented) The method of claim 42 wherein the plasticizer comprises at least one plasticizer selected from the group consisting of: polyethylene glycol; polyethylene oxide; oligomeric lactic acid; a citrate ester; a glucose monoester; a partially fatty acid ester; PEG monolaurate; triacetin; poly(ϵ -caprolactone); poly(hydroxybutyrate); glycerin-1-benzoate-2,3-dilaurate; glycerin-2-benzoate-1,3-dilaurate; a starch; bis(butyl diethylene glycol)adipate; ethylphthalylethyl glycolate; glycerine diacetate monocaprylate; diacetyl monoacyl glycerol; polypropylene glycol; poly(propylene glycol)dibenzoate, dipropylene glycol dibenzoate; glycerol; ethyl phthalyl ethyl glycolate; poly(ethylene adipate)disterate; di-iso-butyl adipate; and any combination thereof.

48. (Previously Presented) The method of claim 42 wherein the acid-releasing degradable material comprises a poly(orthoester).

49. (Previously Presented) A method of using a portion of a gravel pack to degrade a portion of a filter cake comprising the steps of:

combining an acid-releasing degradable material with a solvent or a plasticizer to create a coating solution; wherein the acid-releasing degradable material comprises at least one acid-releasing degradable material selected from the group consisting of: poly(orthoester); a poly(ϵ -caprolactone); a poly(hydroxybutyrate); a substantially water insoluble anhydride; a poly(anhydride); a poly(amino acid); a mixture of one of the above-listed compounds; a copolymer of two or more of the above-listed compounds; and any combination thereof;

coating the coating solution onto gravel on-the-fly to create coated gravel;

introducing the coated gravel to a well bore having a filter cake so that at least a portion of the coated gravel is incorporated in a gravel pack substantially adjacent to the filter cake;

allowing the acid-releasing degradable material to produce acid; and,

allowing the acid to contact and degrade a portion of the filter cake.

50. (Previously Presented) The method of claim 49 wherein the gravel pack compositions comprises from about 0.1% to about 20% acid-releasing degradable material by weight of the gravel particles.

51. (Previously Presented) The method of claim 49 wherein the acid-releasing degradable material comprises a material that is substantially water insoluble such that it degrades over time.

52. (Previously Presented) The method of claim 49 wherein the solvent comprises at least one solvent selected from the group consisting of: acetone; propylene carbonate; di(propylene glycol) methyl ether; di(propylene glycol) propyl ether; di(propylene glycol) butyl ether; di(propylene glycol) methyl ether acetate; isopropyl alcohol; chloroform; dichloromethane; trichloromethane; 1,2-dichlorobenzene; tetrahydrofuran; benzene; acetonitrile; dioxane; dimethylformamide; toluene; ethyl acetate; isoamyl alcohol; N-methylpyrrolidone; xylene; dichloroacetic acid; m-cresol; hexafluoroisopropanol; diphenyl ether; acetonitrile; methanol; ethyl benzene; naphthalene; naphtha; and any combination thereof.

53. (Previously Presented) The method of claim 49 wherein the plasticizer comprises at least one plasticizer selected from the group consisting of: polyethylene glycol; polyethylene oxide; oligomeric lactic acid; a citrate ester; a glucose monoester; a partially fatty acid ester; PEG monolaurate; triacetin; poly(ϵ -caprolactone); poly(hydroxybutyrate); glycerin-1-benzoate-2,3-dilaurate; glycerin-2-benzoate-1,3-dilaurate; a starch; bis(butyl diethylene glycol)adipate; ethylphthalylethyl glycolate; glycerine diacetate monocaprylate; diacetyl monoacyl glycerol; polypropylene glycol; poly(propylene glycol)dibenzoate, dipropylene glycol dibenzoate; glycerol; ethyl phthalyl ethyl glycolate; poly(ethylene adipate)disterate; di-iso-butyl adipate; and any combination thereof.

54. (Previously Presented) The method of claim 49 wherein the acid-releasing degradable material comprises a poly(orthoester).

55. (Previously Presented) A method of degrading filter cake in a subterranean formation comprising the steps of:

- combining an acid-releasing degradable material with a plasticizer to create a coating solution, with the proviso that the plasticizer does not comprise a starch;

- coating the coating solution onto a particulate on-the-fly to create coated particulates;

- placing the coated particulates into a subterranean formation so that at least a portion of the coated particulates become incorporated in a pack substantially adjacent to a filter cake;

- allowing the acid-releasing degradable material to produce acid; and

allowing the acid to contact and degrade a portion of the filter cake.

56. (Previously Presented) The method of claim 55 wherein the filter cake comprises a filter cake on the walls of a well bore or a filter cake on the walls of a fracture.

57. (Previously Presented) The method of claim 55 wherein the particulates are coated with from about 0.1% to about 20% acid-releasing degradable material by weight of the particulates.

58. (Previously Presented) The method of claim 55 wherein acid-releasing degradable material comprises a material that is substantially water insoluble and that degrades over time in an aqueous environment.

59. (Previously Presented) The method of claim 55 wherein the acid-releasing degradable material comprises at least one acid-releasing degradable material selected from the group consisting of: a polyester, a poly(orthoester); a lactide, a poly(lactide); a glycolide; a poly(glycolide); a poly(ϵ -caprolactone); a poly(hydroxybutyrate); a substantially water insoluble anhydride; a poly(anhydride); a poly(amino acid); a mixture of one of the above-listed compounds; a copolymer of two or more of the above-listed compounds; and any combination thereof.

60. (Previously Presented) The method of claim 55 wherein the plasticizer comprises at least one plasticizer selected from the group consisting of: polyethylene glycol; polyethylene oxide; oligomeric lactic acid; a citrate ester; a glucose monoester; a partially fatty acid ester; PEG monolaurate; triacetin; poly(ϵ -caprolactone); poly(hydroxybutyrate); glycerin-1-benzoate-2,3-dilaurate; glycerin-2-benzoate-1,3-dilaurate; bis(butyl diethylene glycol)adipate; ethylphthalylethyl glycolate; glycerine diacetate monocaprylate; diacetyl monoacyl glycerol; polypropylene glycol; poly(propylene glycol)dibenzoate, dipropylene glycol dibenzoate; glycerol; ethyl phthalyl ethyl glycolate; poly(ethylene adipate)disterate; di-iso-butyl adipate; and any combination thereof.

61. (Previously Presented) The method of claim 55 wherein the acid-releasing degradable material comprises a poly(orthoester).

APPENDIX B: EVIDENCE

None

APPENDIX C: RELATED PROCEEDINGS

None

APPENDIX D: SPECIFICATION AS FILED

**ON-THE FLY COATING OF ACID-RELEASING DEGRADABLE
MATERIAL ONTO A PARTICULATE**

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation-in-part of U.S. Application Serial No. 10/641,242, which was filed on 8/14/2003.

BACKGROUND OF THE INVENTION

[0002] The present invention relates to methods and compositions for treating subterranean formations, and more specifically, to improved methods and compositions for degrading filter cake deposited in a subterranean formation.

[0003] Filter cake, the residue deposited on a permeable medium when servicing fluids contact the medium under a pressure, is formed in a variety of subterranean operations such as drilling, fracturing, and gravel packing. A filter cake is often desirable, at least temporarily, in subterranean operations as it may act to stem the flow of a servicing fluid from its desired location, to the surrounding subterranean formation. For instance, where the servicing fluid is a drilling fluid, a filter cake formed on the wall of the well bore may act to keep the drilling fluid in its desired location, in the annulus between the well bore and the drill pipe, rather than allowing the drilling fluid to leach off into the surrounding formation. Loss of drilling, fracturing, gravel transport and other servicing fluids into the formation represents an increased expense and, if too much fluid is lost, the attendant increase in damage to the producing zones in the formation. Moreover, the presence of a filter cake may add strength and stability to the formation surfaces on which the filter cake forms, as in the case of soft sandstone formations.

[0004] Filter cakes may be formed during drilling and fracturing operations. Once a well bore is established, the producing zones along the well bore may be treated to increase their production rate. One such production stimulation treatment involves hydraulically fracturing the formation with a viscous treating fluid to create one or more cracks or "fractures." As a fracture is created, a portion of the fluid contained in the viscous fracturing fluid leaks off into the formation and creates a filter cake comprising deposited viscosifying agent and fluid loss control agent on the walls of the fracture and the formation. The filter cake acts as a physical barrier to

liquid travel that, as described above, helps reduce fluid loss into the producing zone. The filter cake may also present a barrier to flow of liquid from the zone, thus, after the fracturing operation has been completed, the filter cake generally needs to be removed to maximize oil and/or gas production.

[0005] Sand control operations, such as gravel packing, are also common after a well bore is drilled. One common type of gravel packing operation involves placing a gravel pack screen in the well bore and packing the surrounding annulus between the screen and the well bore with gravel of a specific size designed to prevent the passage of formation sand. The gravel pack screen is generally a filter assembly used to retain the gravel placed during gravel pack operation. A wide range of sizes and screen configurations are available to suit the characteristics of the gravel pack sand used. Similarly, a wide range of sizes of gravel is available to suit the characteristics of the unconsolidated or poorly consolidated particulates in the subterranean formation. The resulting structure presents a barrier to migrating sand from the formation while still permitting fluid flow. When installing the gravel pack, the gravel is carried to the formation in the form of a slurry by mixing the gravel with a transport fluid. Gravel packs act, *inter alia*, to stabilize the formation while causing minimal impairment to well productivity. The gravel, *inter alia*, acts to prevent the particulates from occluding the screen or migrating with the produced fluids, and the screen, *inter alia*, acts to prevent the gravel from entering the production tubing. Often, gravel packs are placed along a well bore having a filter cake on its walls.

[0006] While filter cakes may be beneficial, it is generally necessary to remove filter cakes from producing zones before the well is placed onto production. One known method for the removal of filter cakes from producing formations involves including an acid-soluble particulate solid bridging agent for bridging over the formation pores in the drilling, fracturing, gravel transport or other servicing fluid that forms the filter cake. Such an acid-soluble filter cake could then be removed by placing a strongly acidic acid solution in contact with the filter cake and allowing that solution to remain in contact for a period of time sufficient to dissolve the filter cake.

[0007] One consideration in removing a deposited filter cake from a subterranean well bore formation involves the timing of such removal. For instance, in situations where sand control of the formation is a concern, a filter cake offers some degree of control over

unconsolidated particulates in the subterranean formation while placing the gravel pack. For example, if the filter cake is removed prior to gravel packing, the unconsolidated particulates are not controlled and well bore stability problems may arise causing the collapse of the bore hole and preventing the installation of a gravel pack. While installing the screen and placing the gravel before removing the filter cake helps control unconsolidated particulates and maintain bore hole stability, it also makes the filter cake itself more difficult to remove. This is because the screen and gravel represents a physical barrier between the filter cake on walls of the well bore and the acidic fluid used to remove the filter cake.

[0008] One conventional method that attempts to overcome that problem involves placing a breaker (*e.g.*, an oxidizer, ester, enzyme, or the like) in the fracturing, transport or other servicing fluid that creates and/or treats the filter cake in hopes that the breaker will permeate the filter cake and break it down. However, because the breaker is dissolved in the servicing fluid and not all of the servicing fluid remains in the subterranean formation *inter alia*, while circulating a gravel pack, much of the breaker that is used gets circulated out of the well bore and does not interact with the filter cake as desired.

[0009] More recently, it has been found that acid-releasing degradable material may be coated onto a particulate and act at a delayed rate to produce acid such that the particulate may be placed in the subterranean formation adjacent to the filter cake before a substantial amount of acid is released. In such methods known in the art, the acid-releasing degradable material had to be coated onto the particulate in a controlled environment off-site from the well head. The material then had to be coated onto various types and sizes of gravel/proppant, stored, and transported before it could be used in a subterranean formation.

SUMMARY OF THE INVENTION

[0010] The present invention relates to methods and compositions for treating subterranean formations, and more specifically, to improved methods and compositions for degrading filter cake deposited on a subterranean formation.

[0011] One embodiment of the present invention provides a method of creating particulates coated with acid-releasing degradable material on-the-fly comprising the step of: combining an acid-releasing degradable material with a solvent or a plasticizer to create a coating solution; and, coating the coating solution onto a particulate on-the-fly to create coated particulates.

[0012] Another embodiment of the present invention provides a method of degrading filter cake in a subterranean formation comprising the steps of: combining an acid-releasing degradable material with a solvent or a plasticizer to create a coating solution; coating the coating solution onto a particulate on-the-fly to create coated particulates; placing the coated particulates into a subterranean formation so that they form a pack substantially adjacent to a filter cake; allowing the low molecular weight acid-releasing degradable material to produce acid; and allowing the acid to contact and degrade a portion of the filter cake.

[0013] Still another embodiment of the present invention provides a gravel pack comprising gravel particles coated on-the-fly with an acid-releasing degradable material.

[0014] The objects, features, and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of the preferred embodiments that follows.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0015] The present invention relates to methods and compositions for treating subterranean formations, and more specifically, to improved methods and compositions for degrading filter cake deposited on a subterranean formation.

[0016] Certain embodiments of the compositions of the present invention comprise particulates coated on-the-fly with an acid-releasing degradable material that releases acid over time. The released acid may be used to degrade an acid-degradable filter cake substantially adjacent to the coated particulates. In some embodiments the acid-releasing degradable material used to coat the particulates acts at a delayed rate to produce acid such that the particles may be placed in the subterranean formation adjacent to the filter cake before a substantial amount of acid is released. The compositions and methods of the present invention are suitable for use in removing any filter cake that degrades in the presence of an acid.

[0017] Any particulate material suitable for use in conjunction with subterranean applications is suitable for use as the particulate in the compositions and methods of the present invention. Natural sand, quartz sand, particulate garnet, glass, ground walnut hulls, nylon pellets, bauxite, ceramics, polymeric materials, or the like are all suitable. Suitable sizes range from 4 to 100 U.S. mesh, in certain preferred embodiments the sizes range from 10 to 70 US mesh. The particulate material of the present invention may be used as gravel particles used in sand control operations, as proppant particles used in fracturing operations, or as any other particulate employed in subterranean operations that may be placed substantially adjacent to a filter cake.

[0018] Acid-releasing degradable materials that may be used in conjunction with the present invention are those materials that can be coated onto a particulate on-the-fly and that are substantially water insoluble such that they degrade over time, rather than instantaneously, to produce an acid.

[0019] Moreover, in order for an acid-releasing degradable material to be suitable for on-the-fly coating onto a particulate, it must be in a substantially liquid, flowable form. Solvents can be used for this purpose. Such suitable solvents include, but are not limited to, acetone, propylene carbonate, di(propylene glycol) methyl ether, di(propylene glycol) propyl ether, di(propylene glycol) butyl ether, di(propylene glycol) methyl ether acetate, isopropyl alcohol, chloroform, dichloromethane, trichloromethane, 1,2-dichlorobenzene, tetrahydrofuran, benzene,

acetonitrile, dioxane, dimethylformamide, toluene, ethyl acetate, isoamyl alcohol, N-methylpyrrolidone, xylenes, dichloroacetic acid, m-cresol, hexafluoroisopropanol, diphenyl ether, acetonitrile, methanol, ethyl benzene, naphthalene, naphtha and combinations thereof. As an alternative to a solvent, a plasticizer also may be used to make the polymer more flowable for the coating process. Examples of plasticizers useful for this purpose include, but are not limited to, polyethylene glycol; polyethylene oxide; oligomeric lactic acid; citrate esters (such as tributyl citrate oligomers, triethyl citrate, acetyltributyl citrate, acetyltriethyl citrate, 25% by weight after the phase separate); glucose monoesters; partially fatty acid esters; PEG monolaurate; triacetin; poly(ϵ -caprolactone); poly(hydroxybutyrate); glycerin-1-benzoate-2,3-dilaurate; glycerin-2-benzoate-1,3-dilaurate; starch; bis(butyl diethylene glycol)adipate; ethylphthalylethyl glycolate; glycerine diacetate monocaprylate; diacetyl monoacyl glycerol; polypropylene glycol (and epoxy derivatives thereof); poly(propylene glycol)dibenzoate, dipropylene glycol dibenzoate; glycerol; ethyl phthalyl ethyl glycolate; poly(ethylene adipate)disterate; di-iso-butyl adipate; and combinations thereof.

[0020] Generally, suitable acid-releasing degradable materials include polyesters; poly(orthoesters); aliphatic polyesters; lactides, poly(lactides); glycolides; poly(glycolides); poly(ϵ -caprolactone); poly(hydroxybutyrate); substantially water insoluble anhydrides; poly(anhydrides); poly(amino acids); and mixtures and copolymers of the same. The acid-releasing degradable material chosen must be substantially soluble in the chosen solvent. While no particular molecular weight is required, lower molecular weight materials may be more easily soluble. By way of example, polylactides having a molecular weight of less than about 3,000 are generally soluble in propylene carbonate while polylactides having a molecular weight of 50,000 generally are not. Copolymerization may also be used to facilitate solubility in a suitable solvent. By way of example, copolymers of lactide and glycolide will be soluble in di(propylene glycol) methyl ether at molecular weights where a polylactide material of the same molecular weight would not be soluble. Amorphous polymers are generally more soluble in solvents and this property can be considered in choosing a material for coating. It is within the ability of one skilled in the art, with the benefit of this disclosure, to select an acid-releasing degradable material suitable for use in the present invention.

[0021] Polymers suitable for use as an acid-releasing degradable material of the present invention may be considered degradable if the degradation is due, *inter alia*, to chemical and/or

radical process such as hydrolysis, oxidation, or enzymatic decomposition. The degradability of a polymer depends at least in part on its backbone structure, type of repetitive unit, composition, sequence, length, molecular geometry, molecular weight, morphology (*e.g.*, crystallinity, size of spherulites, and orientation), hydrophilicity, hydrophobicity, surface area, and additives. Also, the environment to which the polymer is subjected may affect how it degrades, *e.g.*, temperature, presence of moisture, oxygen, microorganisms, enzymes, pH, and the like.

[0022] Blends of certain acid-releasing degradable materials may also be suitable. One example of a suitable blend of materials includes a blend of a poly(lactic acid) and lactide. Other materials that undergo degradation and produce acid may also be suitable, if the products of the degradation do not undesirably interfere with either the subterranean treatment being performed or the subterranean formation.

[0023] In choosing the appropriate acid-releasing degradable material, one should consider the degradation products that will result. Also, these degradation products should not adversely affect other operations or components. The conditions of the well, *e.g.*, well bore temperature and environmental factors, must also be considered when choosing an acid-releasing degradable material. For instance, polyesters have been found to be suitable for well bore temperatures in the range of 60°F to 400°F. Generally, smaller molecule acid-releasing degradable materials are suitable for use in lower temperature application and larger molecule acid-releasing degradable materials are suitable for use in higher-temperature applications. By way of example, lactide is suitable for temperatures below 120 F and 3,000 molecular weight polylactide for temperatures above 180 F. Copolymers of lactide and glycolide are suitable for use in the 120 F to 180 F. It is within the ability of one skilled in the art, with the benefit of this disclosure, to select a suitable acid-releasing degradable material.

[0024] When used in the present invention, a preferable result is achieved if the degradable material degrades slowly over time as opposed to instantaneously. Even more preferable results have been obtained when the degradable material does not substantially degrade until after the subterranean treatment, such as a gravel packing or fracturing operation, has been substantially completed.

[0025] The acid-releasing degradable material of the present invention may be coated onto particulate material by any means known in the art. In one embodiment, the particles may be coated with the acid-releasing degradable material "on-the-fly." The term "on-the-fly" is used

herein to mean that one flowing stream is continuously introduced into another flowing stream so that the streams are combined and mixed while continuing to flow as a single stream as part of the on-going treatment at the job site. Such mixing can also be described as "real-time" mixing. One such on-the-fly mixing method would involve continuously conveying the particles and the acid-releasing degradable material to a mixing vessel. Once inside the mixing vessel, the particles would be coated with the acid-releasing degradable material and continuously removed from the mixing vessel. In that situation, a sand screw could be used both to aid in mixing the particulates, be they gravel, proppant, or some other particulate, with the acid-releasing degradable material and to remove the acid-releasing degradable material-coated particles from the mixing tank. As is well understood by those skilled in the art, batch or partial batch mixing may also be used to accomplish such coating.

[0026] In some embodiments of the present invention the particle material, such as gravel in a gravel packing operation or proppant in a fracturing operation, is coated with from about 0.1% to about 20% acid-releasing degradable material by weight of the gravel particles, more preferably from about 0.5% to about 10% acid-releasing degradable material by weight of the gravel particles and most preferably from about 1% to about 8% acid-releasing degradable material by weight of the particulate material. In some embodiments of the present invention, all of the particles used in the subterranean operation are coated with an acid-releasing degradable material of the present invention. In other embodiments, only a portion of the particles is coated. Where the percentage of particles coated is less than 100%, it may be desirable to coat a higher percentage of the acid-releasing degradable material on the coated particles. It is within the ability of one skilled in the art to determine the amount of acid-releasing degradable material that will be necessary to sufficiently degrade the filter cake and to coat enough particles with enough acid-releasing degradable material to achieve that goal.

[0027] Where the coated particles of the present invention are used in a sand control operation such as gravel packing, the gravel pack may be formed using any technique known in the art. In one technique, gravel particles at least partially coated with an acid-releasing material are slurried into a delivery fluid and pumped into the well bore having a filter cake deposited thereon and substantially adjacent to the zone of the subterranean formation that has been fitted with a gravel pack screen. The gravel material is separated from the slurry as the delivery fluid is forced into the well bore and through the screen. The gravel particles are not able to flow

through the mesh of the screen and are left behind, thus forming a gravel pack. In a gravel pack formed from such coated particles, the acid-releasing degradable material substantially degrades the adjacent filter cake.

[0028] Similarly, where the coated particles of the present invention are used in a fracturing operation, the proppant pack formed inside the fracture with the coated particles of the present invention may be formed using any technique known in the art. In one technique, proppant particles at least partially coated with an acid-releasing material are slurried into a fracturing fluid and pumped into a fractured subterranean formation. The proppant particles are then placed in the fracture and form a proppant pack substantially adjacent to walls of the fracture. Once the proppant pack is substantially formed, the acid-releasing degradable material produces a sufficient amount of acid at least to partially degrade the filter cake on the walls of the fracture.

[0029] To facilitate a better understanding of the present invention, the following example of a preferred embodiment is given. In no way should the following example be read to limit the scope of the invention.

EXAMPLE

[0030] A 6100 molecular weight copolymer of 50% lactic acid and 50% glycolic acid was synthesized. The copolymer was then dissolved in propylene carbonate to a 50/50% concentration of polymer to solvent. The polymer/solvent was coated onto 20/40 Carbolite® proppant at a 4% concentration by weight of the proppant. A filter cake was deposited on a 35 micron Aloxite core in a Fann HPHT Filtration Cell from a drill-in fluid formulated using a 10% sodium chloride base fluid with 0.2% xanthan, 1.9% starch, 6.7% 5 micron median diameter calcium carbonate, 16.7% 25 micron median diameter calcium carbonate 0.025% sodium hydroxide. Once the filter cake was formed, with 500 psi differential pressure at 150 F for 60 minutes, the excess drill-in fluid was removed from the test chamber and replaced with 141 grams of the coated proppant and 64 mL of 10% sodium chloride solution. The cell was heated to 160 F with 50 psi differential pressure and the filtrate rate was monitored. The filtrate rate averaged around 2 mL/hr for the first 9 hours indicating the filter cake was still intact. At around 9 hours, the filtrate rate began to increase and was around 300 mL/hr within about 5 minutes of the point of the increase. The increase flow rate is an indication of filter cake degradation.

[0031] Therefore, the present invention is well adapted to carry out the objects and attain the ends and advantages mentioned as well as those that are inherent therein. While numerous changes may be made by those skilled in the art, such changes are encompassed within the spirit and scope of this invention as defined by the appended claims.

What is claimed is:

1. A method of creating particulates coated with acid-releasing degradable material on-the-fly comprising the step of:

combining an acid-releasing degradable material with a solvent or a plasticizer to create a coating solution; and,

coating the coating solution onto a particulate on-the-fly to create coated particulates.

2. The method of claim 1 wherein the particulates are coated with from about 0.1% to about 20% low molecular weight acid-releasing degradable material by weight of the particulates.

3. The method of claim 1 wherein the low molecular weight acid-releasing degradable material comprises a material that is substantially water insoluble and that degrades over time in an aqueous environment.

4. The method of claim 1 wherein the acid-releasing degradable material comprises a polyester; a poly(orthoester); an aliphatic polyester; a lactide, a poly(lactide); a glycolide; a poly(glycolide); a poly(ϵ -caprolactone); a poly(hydroxybutyrate); a substantially water insoluble anhydrides; a poly(anhydride); a poly(amino acids); a mixture of one of the above-listed compounds; or a copolymer of two or more of the above-listed compounds.

5. The method of claim 1 wherein the solvent comprises acetone, propylene carbonate, di(propylene glycol) methyl ether, di(propylene glycol) propyl ether, di(propylene glycol) butyl ether, di(propylene glycol) methyl ether acetate, isopropyl alcohol, chloroform, dichloromethane, trichloromethane, 1,2-dichlorobenzene, tetrahydrofuran, benzene, acetonitrile, dioxane, dimethylformamide, toluene, ethyl acetate, isoamyl alcohol, N-methylpyrrolidone, xylenes, dichloroacetic acid, m-cresol, hexafluoroisopropanol, diphenyl ether, acetonitrile, methanol, ethyl benzene, naphthalene, naphtha, or combinations thereof.

6. The method of claim 1 wherein the plasticizer comprises polyethylene glycol; polyethylene oxide; oligomeric lactic acid; citrate esters; glucose monoesters; partially fatty acid esters; PEG monolaurate; triacetin; poly(ϵ -caprolactone); poly(hydroxybutyrate); glycerin-1-benzoate-2,3-dilaurate; glycerin-2-benzoate-1,3-dilaurate; starch; bis(butyl diethylene glycol)adipate; ethylphthalylethyl glycolate; glycerine diacetate monocaprylate; diacetyl monoacyl glycerol; polypropylene glycol; poly(propylene glycol)dibenzoate, dipropylene glycol

dibenzoate; glycerol; ethyl phthalyl ethyl glycolate; poly(ethylene adipate)disterate; di-iso-butyl adipate; or combinations thereof.

7. A method of degrading filter cake in a subterranean formation comprising the steps of:

combining an acid-releasing degradable material with a solvent or a plasticizer to create a coating solution;

coating the coating solution onto a particulate on-the-fly to create coated particulates;

placing the coated particulates into a subterranean formation so that they form a pack substantially adjacent to a filter cake;

allowing the low molecular weight acid-releasing degradable material to produce acid; and

allowing the acid to contact and degrade a portion of the filter cake.

8. The method of claim 7 wherein the filter cake comprises a filter cake on the walls of a well bore or a filter cake on the walls of a fracture.

9. The method of claim 7 wherein the particulates are coated with from about 0.1% to about 20% low molecular weight acid-releasing degradable material by weight of the particulates.

10. The method of claim 7 wherein the low molecular weight acid-releasing degradable material comprises a material that is substantially water insoluble and that degrades over time in an aqueous environment.

11. The method of claim 7 wherein the low molecular weight acid-releasing degradable material comprises a polyester; a poly(orthoester); an aliphatic polyester; a lactide, a poly(lactide); a glycolide; a poly(glycolide); a poly(ϵ -caprolactone); a poly(hydroxybutyrate); a substantially water insoluble anhydrides; a poly(anhydride); a poly(amino acids); a mixture of one of the above-listed compounds; or a copolymer of two or more of the above-listed compounds.

12. The method of claim 7 wherein the solvent comprises acetone, propylene carbonate, di(propylene glycol) methyl ether, di(propylene glycol) propyl ether, di(propylene glycol) butyl ether, di(propylene glycol) methyl ether acetate, isopropyl alcohol, chloroform, dichloromethane, trichloromethane, 1,2-dichlorobenzene, tetrahydrofuran, benzene, acetonitrile, dioxane, dimethylformamide, toluene, ethyl acetate, isoamyl alcohol, N-methylpyrrolidone,

xylene, dichloroacetic acid, m-cresol, hexafluoroisopropanol, diphenyl ether, acetonitrile, methanol, ethyl benzene, naphthalene, naphtha, or combinations thereof.

13. The method of claim 7 wherein the plasticizer comprises polyethylene glycol; polyethylene oxide; oligomeric lactic acid; citrate esters; glucose monoesters; partially fatty acid esters; PEG monolaurate; triacetin; poly(ϵ -caprolactone); poly(hydroxybutyrate); glycerin-1-benzoate-2,3-dilaurate; glycerin-2-benzoate-1,3-dilaurate; starch; bis(butyl diethylene glycol)adipate; ethylphthalylethyl glycolate; glycerine diacetate monocaprylate; diacetyl monoacyl glycerol; polypropylene glycol; poly(propylene glycol)dibenzoate, dipropylene glycol dibenzoate; glycerol; ethyl phthalyl ethyl glycolate; poly(ethylene adipate)disterate; di-iso-butyl adipate; or combinations thereof.

14. A method of using a portion of a gravel pack to degrade a portion of a filter cake comprising the steps of

combining an acid-releasing degradable material with a solvent or a plasticizer to create a coating solution;

coating the coating solution onto gravel on-the-fly to create coated gravel;

introducing the coated gravel to a well bore having a filter cake so that the coated gravel forms a gravel pack substantially adjacent to the filter cake;

allowing the acid-releasing degradable material to produce acid; and,

allowing the acid to contact and degrade a portion of the filter cake.

15. The method of claim 14 wherein the gravel pack compositions comprises from about 0.1% to about 20% acid-releasing degradable material by weight of the gravel particles.

16. The method of claim 14 wherein the acid-releasing degradable material comprises a material that is substantially water insoluble such that it degrades over time.

17. The method of claim 14 wherein the acid-releasing degradable material comprises a polyester; a poly(orthoester); an aliphatic polyester; a lactide, a poly(lactide); a glycolide; a poly(glycolide); a poly(ϵ -caprolactone); a poly(hydroxybutyrate); a substantially water insoluble anhydrides; a poly(anhydride); a poly(amino acids); a mixture of one of the above-listed compounds; or a copolymer of two or more of the above-listed compounds.

18. The method of claim 14 wherein the solvent comprises acetone, propylene carbonate, di(propylene glycol) methyl ether, di(propylene glycol) propyl ether, di(propylene glycol) butyl ether, di(propylene glycol) methyl ether acetate, isopropyl alcohol, chloroform, dichloromethane, trichloromethane, 1,2-dichlorobenzene, tetrahydrofuran, benzene, acetonitrile, dioxane, dimethylformamide, toluene, ethyl acetate, isoamyl alcohol, N-methylpyrrolidone, xylenes, dichloroacetic acid, m-cresol, hexafluoroisopropanol, diphenyl ether, acetonitrile, methanol, ethyl benzene, naphthalene, naphtha, or combinations thereof.

19. The method of claim 14 wherein the plasticizer comprises polyethylene glycol; polyethylene oxide; oligomeric lactic acid; citrate esters; glucose monoesters; partially fatty acid esters; PEG monolaurate; triacetin; poly(ϵ -caprolactone); poly(hydroxybutyrate); glycerin-1-benzoate-2,3-dilaurate; glycerin-2-benzoate-1,3-dilaurate; starch; bis(butyl diethylene glycol)adipate; ethylphthalylethyl glycolate; glycerine diacetate monocaprylate; diacetyl monoacyl glycerol; polypropylene glycol; poly(propylene glycol)dibenzoate, dipropylene glycol

dibenzoate; glycerol; ethyl phthalyl ethyl glycolate; poly(ethylene adipate)disterate; di-iso-butyl adipate; or combinations thereof.

20. A method of using a portion of a proppant pack to degrade filter cake comprising the steps of:

combining an acid-releasing degradable material with a solvent or a plasticizer to create a coating solution;

coating the coating solution onto proppant on-the-fly to create coated proppant;

introducing the coated proppant to a fracture so that a proppant pack forms against walls of the fracture wherein a wall of the fracture has a filter cake thereon;

allowing the acid-releasing degradable material to produce acid; and,

allowing the acid to contact and degrade a portion of the filter cake.

21. The method of claim 20 wherein the proppant pack composition comprises from about 0.1% to about 20% acid-releasing degradable material by weight of the gravel particles.

22. The method of claim 20 wherein the acid-releasing degradable material comprises a material that is substantially water insoluble such that it degrades over time.

23. The method of claim 20 wherein the acid-releasing degradable material comprises a polyester; a poly(orthoester); an aliphatic polyester; a lactide, a poly(lactide); a glycolide; a poly(glycolide); a poly(ϵ -caprolactone); a poly(hydroxybutyrate); a substantially water insoluble anhydrides; a poly(anhydride); a poly(amino acids); a mixture of one of the above-listed compounds; or a copolymer of two or more of the above-listed compounds.

24. The method of claim 20 wherein the solvent comprises acetone, propylene carbonate, di(propylene glycol) methyl ether, di(propylene glycol) propyl ether, di(propylene glycol) butyl ether, di(propylene glycol) methyl ether acetate, isopropyl alcohol, chloroform, dichloromethane, trichloromethane, 1,2-dichlorobenzene, tetrahydrofuran, benzene, acetonitrile, dioxane, dimethylformamide, toluene, ethyl acetate, isoamyl alcohol, N-methylpyrrolidone, xylenes, dichloroacetic acid, m-cresol, hexafluoroisopropanol, diphenyl ether, acetonitrile, methanol, ethyl benzene, naphthalene, naphtha, or combinations thereof.

25. The method of claim 20 wherein the plasticizer comprises polyethylene glycol; polyethylene oxide; oligomeric lactic acid; citrate esters; glucose monoesters; partially fatty acid esters; PEG monolaurate; triacetin; poly(ϵ -caprolactone); poly(hydroxybutyrate); glycerin-1-benzoate-2,3-dilaurate; glycerin-2-benzoate-1,3-dilaurate; starch; bis(butyl diethylene glycol)adipate; ethylphthalylethyl glycolate; glycerine diacetate monocaprylate; diacetyl monoacyl glycerol; polypropylene glycol; poly(propylene glycol)dibenzoate, dipropylene glycol

dibenzoate; glycerol; ethyl phthalyl ethyl glycolate; poly(ethylene adipate)disterate; di-iso-butyl adipate; or combinations thereof,

26. A gravel pack comprising gravel particles coated on-the-fly with an acid-releasing degradable material.

27. The gravel pack of claim 26 wherein the gravel pack compositions comprises from about 0.1% to about 20% acid-releasing degradable material by weight of the gravel particles.

28. The gravel pack of claim 26 wherein the acid-releasing degradable material comprises a material that is substantially water insoluble such that it degrades over time.

29. The gravel pack of claim 26 wherein the acid-releasing degradable material comprises a polyester; a poly(orthoester); an aliphatic polyester; a lactide, a poly(lactide); a glycolide; a poly(glycolide); a poly(ϵ -caprolactone); a poly(hydroxybutyrate); a substantially water insoluble anhydrides; a poly(anhydride); a poly(amino acids); a mixture of one of the above-listed compounds; or a copolymer of two or more of the above-listed compounds.

30. The gravel pack of claim 26 wherein the acid-releasing degradable material further comprises a solvent.

31. The gravel pack of claim 30 wherein the solvent comprises acetone, propylene carbonate, di(propylene glycol) methyl ether, di(propylene glycol) propyl ether, di(propylene glycol) butyl ether, di(propylene glycol) methyl ether acetate, isopropyl alcohol, chloroform, dichloromethane, trichloromethane, 1,2-dichlorobenzene, tetrahydrofuran, benzene, acetonitrile, dioxane, dimethylformamide, toluene, ethyl acetate, isoamyl alcohol, N-methylpyrrolidone, xylenes, dichloroacetic acid, m-cresol, hexafluoroisopropanol, diphenyl ether, acetonitrile, methanol, ethyl benzene, naphthalene, naphtha, or combinations thereof.

32. The gravel pack of claim 26 wherein the acid-releasing degradable material further comprises a plasticizer.

33. The gravel pack of claim 32 wherein the plasticizer comprises polyethylene glycol; polyethylene oxide; oligomeric lactic acid; citrate esters; glucose monoesters; partially fatty acid esters; PEG monolaurate; triacetin; poly(ϵ -caprolactone); poly(hydroxybutyrate); glycerin-1-benzoate-2,3-dilaurate; glycerin-2-benzoate-1,3-dilaurate; starch; bis(butyl diethylene glycol)adipate; ethylphthalylethyl glycolate; glycerine diacetate monocaprylate; diacetyl monoacyl glycerol; polypropylene glycol; poly(propylene glycol)dibenzoate, dipropylene glycol dibenzoate; glycerol; ethyl phthalyl ethyl glycolate; poly(ethylene adipate)disterate; di-iso-butyl adipate; or combinations thereof.

34. A proppant pack comprising proppant particles coated on-the-fly with an acid-releasing degradable material.

35. The proppant pack of claim 34 wherein the proppant pack compositions comprises from about 0.1% to about 20% acid-releasing degradable material by weight of the gravel particles.

36. The proppant pack of claim 34 wherein the acid-releasing degradable material comprises a material that is substantially water insoluble such that it degrades over time.

37. The proppant pack of claim 34 wherein the acid-releasing degradable material comprises a polyester; a poly(orthoester); an aliphatic polyester; a lactide, a poly(lactide); a glycolide; a poly(glycolide); a poly(ϵ -caprolactone); a poly(hydroxybutyrate); a substantially water insoluble anhydrides; a poly(anhydride); a poly(amino acids); a mixture of one of the above-listed compounds; or a copolymer of two or more of the above-listed compounds.

38. The proppant pack of claim 34 wherein the acid-releasing degradable material further comprises a solvent.

39. The proppant pack of claim 38 wherein the solvent comprises acetone, propylene carbonate, di(propylene glycol) methyl ether, di(propylene glycol) propyl ether, di(propylene glycol) butyl ether, di(propylene glycol) methyl ether acetate, isopropyl alcohol, chloroform, dichloromethane, trichloromethane, 1,2-dichlorobenzene, tetrahydrofuran, benzene, acetonitrile, dioxane, dimethylformamide, toluene, ethyl acetate, isoamyl alcohol, N-methylpyrrolidone, xylenes, dichloroacetic acid, m-cresol, hexafluoroisopropanol, diphenyl ether, acetonitrile, methanol, ethyl benzene, naphthalene, naphtha, or combinations thereof.

40. The proppant pack of claim 34 wherein the acid-releasing degradable material further comprises a plasticizer.

41. The proppant pack of claim 40 wherein the plasticizer comprises polyethylene glycol; polyethylene oxide; oligomeric lactic acid; citrate esters; glucose monoesters; partially fatty acid esters; PEG monolaurate; triacetin; poly(ϵ -caprolactone); poly(hydroxybutyrate); glycerin-1-benzoate-2,3-dilaurate; glycerin-2-benzoate-1,3-dilaurate; starch; bis(butyl diethylene glycol)adipate; ethylphthalylethyl glycolate; glycerine diacetate monocaprylate; diacetyl monoacyl glycerol; polypropylene glycol; poly(propylene glycol)dibenzoate, dipropylene glycol dibenzoate; glycerol; ethyl phthalyl ethyl glycolate; poly(ethylene adipate)disterate; di-iso-butyl adipate; or combinations thereof.

ON-THE FLY COATING OF ACID-RELEASING DEGRADABLE MATERIAL ONTO A PARTICULATE

Abstract of the Disclosure

[0032] The present invention relates to methods and compositions for treating subterranean formations, and more specifically, to improved methods and compositions for degrading filter cake deposited on a subterranean formation. One embodiment of the present invention provides a method of creating particulates coated with acid-releasing degradable material on-the-fly comprising the step of: combining an acid-releasing degradable material with a solvent or a plasticizer to create a coating solution; and, coating the coating solution onto a particulate on-the-fly to create coated particulates. Another embodiment of the present invention provides a gravel pack comprising gravel particles coated on-the-fly with an acid-releasing degradable material.

APPENDIX E: SELECTED PRIOR ART RELIED UPON IN REJECTIONS

Contents:

1. U.S. Patent No. 6,209,643 issued to Nguyen *et al.* ("*Nguyen*")
2. U.S. Patent No. 6,458,867 issued to Wang *et al.* ("*Wang*")
3. U.S. Patent No. 6,817,414 issued to Lee *et al.* ("*Lee*")
4. U.S. Patent No. 5,192,615 issued to McDougall *et al.* ("*McDougall*")
5. U.S. Patent No. 6,669,771 to Tokiwa *et al.* ("*Tokiwa*")



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(12) **United States Patent**
Nguyen et al.

(10) Patent No.: **US 6,209,643 B1**
 (45) Date of Patent: **Apr. 3, 2001**

(54) **METHOD OF CONTROLLING PARTICULATE FLOWBACK IN SUBTERRANEAN WELLS AND INTRODUCING TREATMENT CHEMICALS**

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Related U.S. Application Data

(63) Continuation-in-part of application No. 09/188,880, filed on Nov. 9, 1998, now Pat. No. 5,047,772, which is a continuation-in-part of application No. 08/783,050, filed on Jan. 14, 1997, now Pat. No. 5,839,510, which is a continuation-in-part of application No. 08/725,368, filed on Oct. 3, 1996, now Pat. No. 5,787,986, which is a continuation-in-part of application No. 08/510,399, filed on Aug. 2, 1995, now Pat. No. 5,582,249, which is a continuation-in-part of application No. 08/412,668, filed on Mar. 29, 1995, now Pat. No. 5,501,274.

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 507/939; 523/131
 (58) Field of Search 166/276, 279,
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 924, 939; 523/131

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(57) **ABSTRACT**

The present invention provides a method of treating a subterranean formation with a particulate laden fluid whereby particulate flowback is reduced or prevented while also providing a controlled release of a treatment chemical within the formation. The method includes the steps of providing a fluid suspension including a mixture of a particulate, a tackifying compound and a treatment chemical, pumping the suspension into a subterranean formation and depositing the mixture within the formation whereby the tackifying compound retards movement of at least a portion of the particulate within the formation upon flow of fluids from the subterranean formation and said tackifying compound retards release of at least a portion.

19 Claims, No Drawings

METHOD OF CONTROLLING PARTICULATE FLOWBACK IN SUBTERRANEAN WELLS AND INTRODUCING TREATMENT CHEMICALS

CROSS-REFERENCE TO RELATED APPLICATIONS

The present Application is a Continuation-in-Part of U.S. application Ser. No. 09/188,880, filed Nov. 9, 1998, now U.S. Pat. No. 6,047,772 issued Apr. 11, 2000, which is a Continuation-in-Part of U.S. application Ser. No. 08/783,050, filed Jan. 14, 1997, now U.S. Pat. No. 5,839,510, issued Nov. 24, 1998, which is a Continuation-in-Part of U.S. application Ser. No. 08/725,368, filed Oct. 3, 1996, now U.S. Pat. No. 5,787,986, issued Aug. 4, 1998, which is a Continuation-in-Part of U.S. application Ser. No. 08/510,399, filed Aug. 2, 1995, now U.S. Pat. No. 5,582,249 issued Dec. 10, 1996 which is a Continuation-in-Part of U.S. application Ser. No. 08/412,668, filed Mar. 29, 1995, now U.S. Pat. No. 5,501,274 issued Mar. 26, 1996.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to means for recovering hydrocarbons from a subterranean formation and more particularly to a method and means for controlling particulate solids transport during the production of hydrocarbons from a subterranean formation and providing delayed release of treatment chemicals into a subterranean formation in a substantially uniform manner.

2. Brief Description of the Prior Art

Transport of particulate solids during the production of hydrocarbons from a subterranean formation is a continuing problem. The transported solids can erode or cause significant wear in the hydrocarbon production equipment used in the recovery process. The solids also can clog or plug the wellbore thereby limiting or completely stopping fluid production. Further, the transported particulates must be separated from the recovered hydrocarbons adding further expense to the processing. The particulates which are available for transport may be present due to an unconsolidated nature of a subterranean formation and/or as a result of well treatments placing particulates in a wellbore or formation, such as, by gravel packing or propped fracturing.

In the treatment of subterranean formations, it is common to place particulate materials as a filter medium and/or a proppant in the near wellbore area and in fractures extending outwardly from the wellbore. In fracturing operations, proppant is carried into fractures created when hydraulic pressure is applied to these subterranean rock formations to a point where fractures are developed. Proppant suspended in a viscosified fracturing fluid is carried outwardly away from the wellbore within the fractures as they are created and extended with continued pumping. Upon release of pumping pressure, the proppant materials remain in the fractures holding the separated rock faces in an open position forming a channel for flow of formation fluids back to the wellbore.

Proppant flowback is the transport of proppants back into the wellbore with the production of formation fluids following fracturing. This undesirable result causes undue wear on production equipment, the need for separation of solids from the produced hydrocarbons and occasionally also decreases the efficiency of the fracturing operation since the proppant does not remain within the fracture and may limit the width or conductivity of the created flow channel. Proppant flow-

back often may be aggravated by what is described as "aggressive" flowback of the well after a stimulation treatment. Aggressive flowback generally entails flowback of the treatment fluid at a rate of from about 0.001 to about 0.1 barrels per minute (BPM) per perforation of the treatment fluids which were introduced into the subterranean formation. Such flowback rates accelerate or force closure of the formation upon the proppant introduced into the formation. The rapid flowrate can result in large quantities of the proppant flowing back into the wellbore before closure occurs or where inadequate bridging within the formation occurs. The rapid flowback is highly desirable for the operator as it returns a wellbore to production of hydrocarbons significantly sooner than would result from other techniques.

Currently, the primary means for addressing the proppant flowback problem is to employ resin-coated proppants or resin consolidation of the proppant which are not capable of use in aggressive flowback situations. Further, the cost of resin-coated proppant is high, and is therefore used only as a tail-in in the last five to twenty five percent of the proppant placement. Resin-coated proppant is not always effective since there is some difficulty in placing it uniformly within the fractures. Another means showing reasonable effectiveness has been to gradually release fracturing pressure once the fracturing operation has been completed so that fracture closure pressure acting against the proppant builds slowly allowing the proppant particles to stabilize before flowback of the fracturing fluid and the beginning of hydrocarbon production. Such slow return is undesirable, however, since it reduces the production from the wellbore until the treatment fluid is removed.

In unconsolidated formations, it is common to place a filtration bed of gravel in the near-wellbore area in order to present a physical barrier to the transport of unconsolidated formation fines with the production of hydrocarbons. Typically, such so-called "gravel packing operations" involve the pumping and placement of a quantity of gravel and/or sand having a mesh size between about 10 and 60 mesh on the U.S. Standard Sieve Series into the unconsolidated formation adjacent to the wellbore. It is sometimes also desirable to bind the gravel particles together in order to form a porous matrix through which formation fluids can pass while straining out and retaining the bulk of the unconsolidated sand and/or fines transported to the near wellbore area by the formation fluids. The gravel particles may constitute a resin-coated gravel which is either partially cured and subsequently completes curing or can be cured by an overflush of a chemical binding agent once the gravel is in place. It has also been known to add various hardenable binding agents or hardenable adhesives directly to an overflush of unconsolidated gravel in order to bind the particles together.

U.S. Pat. Nos. 5,330,005, 5,439,055 and 5,501,275 disclose a method for overcoming the difficulties of resin coating proppants or gravel packs by the incorporation of a fibrous material in the fluid with which the particulates are introduced into the subterranean formation. The fibers generally have a length ranging upwardly from about 2 millimeters and a diameter of from about 6 to about 200 microns. Fibrillated fibers of smaller diameter also may be used. The fibers are believed to act to bridge across constrictions and orifices in the proppant pack and form a mat or framework which holds the particulates in place thereby limiting particulate flowback. The fibers typically result in a 25 percent or greater loss in permeability of the proppant pack that is created in comparison to a pack without the fibers.

While this technique may function to limit some flowback, it fails to secure the particulates to one another in the manner achieved by use of resin coated particulates.

U.S. Pat. No. 5,501,274 discloses a method for reducing proppant flowback by the incorporation of thermoplastic material in particulate, ribbon or flake form with the proppant. Upon deposition of the proppant and thermoplastic material in the formation, the thermoplastic material softens and causes particulates adjacent the material to adhere to the thermoplastic creating agglomerates. The agglomerates then bridge with the other agglomerates and other particulates to prevent flowback from the formation.

It would be desirable to provide a more permanent method which will bind greater numbers of particles of the particulate to one another whereby agglomerates may be formed which would further assist in preventing movement or flowback of particulates from a wellbore or formation without significantly reducing the permeability of the particulate pack during aggressive flowback of treatment fluids.

It is also desirable to provide a method by which a substantially uniform release of a treatment chemical such as a gel breaker, scale inhibitor, biocide, corrosion inhibitor, paraffin inhibitor or other treatment chemical may be effected within a proppant pack in a subterranean formation. It is also desirable to be able to control the rate of release of the treatment chemical within the subterranean formation.

BRIEF SUMMARY OF THE INVENTION

The present invention provides a method and fluid for treating a subterranean formation and uniformly delivering a controlled release of a treatment chemical to the formation as well as providing a resultant porous particulate pack that inhibits the flow of particulates back through the wellbore during the production of hydrocarbons without significant effects upon the permeability of the particulate pack.

In accordance with the invention, a method of treating a subterranean formation penetrated by a wellbore is provided comprising the steps of providing a fluid suspension including a mixture of particulate material, a material comprising a liquid or solution of a tackifying compound, which coats at least a portion of the particulate upon admixture therewith, a treatment chemical which may be in particulate form or coated upon or in a substrate and, optionally, a hardenable resin, which coats or is coated upon at least a portion of the particulate, pumping the fluid suspension including the coated particulate and treatment chemical through the wellbore and depositing the mixture in the formation. Upon deposition of proppants having been coated with the tackifying compound and optionally the resin material mixture in the formation the coating causes particulate adjacent to the coated material as well as the dispersed treatment chemical particles to adhere to the coated material thereby creating proppant agglomerates which bridge against other particles in the formation to minimize initial particulate flowback and the hardenable resin, when present, subsequently consolidates the particulate.

The coated material is effective in inhibiting the flowback of particulate in a porous pack having a size ranging from about 2 to about 400 mesh in intimate admixture with the tackifying compound coated particulates.

The coated material is effective in consolidating particulate into the form of agglomerates in a formation as a result of a fracturing or gravel packing treatment performed on a subterranean formation during aggressive flowback of the treatment fluid.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, a liquid or solution of a tackifying compound is incorporated in an intimate mixture with a particulate material such as conventional proppants or gravel packing materials together with an optional hardenable resin and introduced into a subterranean formation.

As used in this specification, the term "intimate mixture" will be understood to mean a substantially uniform dispersion of the components in the mixture. The term "simultaneous mixture" will be understood to mean a mixture of components that are blended together in the initial steps of the subterranean formation treatment process or the preparation for the performance of the treatment process.

The coated particulate or proppant material may comprise substantially any substrate material that does not undesirably chemically interact with other components used in treating the subterranean formation. The material may comprise sand, ceramics, glass, sintered bauxite, resin coated sand, resin beads, metal beads and the like. The coated material also may comprise an additional material that is admixed with a particulate and introduced into a subterranean formation to reduce particulate flowback. In this instance the additional substrate material may comprise glass, ceramic, carbon composites, natural or synthetic polymers or metal and the like in the form of fibers, flakes, ribbons, beads, shavings, platelets and the like. In this instance, the additional substrate material generally will be admixed with the particulate in an amount of from about 0.1 to about 5 percent by weight of the particulate.

Surprisingly, it has been found that the additional material also may comprise porous or non-porous substrates upon which a treatment chemical is either absorbed or coated or even particulates or agglomerates of particles of a desired solid treatment chemical which exhibits solubility in the formation fluids upon contact therewith. The additional material may or may not function as a proppant or gravel pack material in the subterranean formation, depending upon the presence or absence of a substrate and its properties. The treatment chemical may comprise gel breakers, such as oxidizers, enzymes or hydrolyzable esters that are capable of producing a pH change in the fluid, scale inhibitors, biocides, corrosion inhibitors, paraffin inhibitors or substantially any other chemical which is soluble in the fluids in the formation at the temperature conditions within the formation within which it is placed. It has been found that the tackifying compound, upon at least partially coating the treatment chemical, retards the dissolution or absorption of the treatment chemical by the formation fluids. The treatment chemical is slowly released within the formation by contact with the fluids present in the formation. The tackifying compound changes the interfacial surface tension effects of the fluids in contact with the treatment chemicals to reduce wetting of the treatment chemicals by the formation fluids thereby reducing the dissolution rate of the chemicals. The presence of the tackifying compound on the particulate or substrate material causes the treatment chemical containing or coated particles to adhere to and remain dispersed within the coated particulate both during mixing, introduction into the formation and upon placement therein. The transported treatment chemicals are not subject to the gravity segregation or premature settling from the particulate material with which it is introduced. Thus, the treatment chemicals can be uniformly dispersed in a proppant pack or gravel pack without undesired segregation or settling to enable uniform release of the treatment chemical within the formation.

The tackifying compound comprises a liquid or a solution of a compound capable of forming at least a partial coating upon the substrate material with which it is admixed prior to or subsequent to placement in the subterranean formation. In some instances, the tackifying compound may be a solid at ambient surface conditions and upon initial admixing with the particulate and after heating upon entry into the wellbore for introduction into the subterranean formation become a melted liquid which at least partially coats a portion of the particulate. Compounds suitable for use as a tackifying compound comprise substantially any compound which when in liquid form or in a solvent solution will form a non-hardening coating, by themselves, upon the particulate which facilitates agglomeration and will increase the continuous critical resuspension velocity of the particulate when contacted by a stream of water as hereinafter described in Example 1 by at least about 30 percent over the particulate alone when present in a 0.5 percent by weight active material concentration. Preferably, the continuous critical resuspension velocity is increased by at least 50 percent over particulate alone. A particularly preferred group of tackifying compounds comprise polyamides which are liquids or in solvent solution at the temperature of the subterranean formation to be treated such that the polyamides are, by themselves, non-hardening when present on the particulates introduced into the subterranean formation. A particularly preferred product is a condensation reaction product comprised of commercially available polyacids and a polyamine. Such commercial products include compounds such as mixtures of C_{14} dibasic acids containing some trimer and higher oligomers and also small amounts of monomer acids which are reacted with polyamines. Other polyacids include trimer acids, synthetic acids produced from fatty acids, maleic anhydride and acrylic acid and the like. Such acid compounds are available from companies such as Witco, Union Carbide, Chemical, and Emery Industries. The reaction products are available from, for example, Champion Chemicals, Inc. and Witco.

In general, the polyamides of the present invention are commercially produced in batchwise processing of polyacids predominately having two or more acid functionalities per molecule with a polyamine. As is well known in the manufacturing industry, the polyacids and polyfunctional amines are introduced into a reactor where, with agitation, the mildly exothermic formation of the amine salt occurs. After mixing, heat is applied to promote endothermic dehydration and formation of the polymer melt by polycondensation. The water of reaction is condensed and removed leaving the polyamide. The molecular weight and final properties of the polymer are controlled by choice and ratio of feedstock, heating rate, and judicious use of monofunctional acids and amines to terminate chain propagation. Generally an excess of polyamine is present to prevent runaway chain propagation. Unreacted amines can be removed by distillation, if desired. Often a solvent, such as an alcohol, is admixed with the final condensation reaction product to produce a liquid solution that can readily be handled. The condensation reaction generally is accomplished at a temperature of from about 225° F. to about 450° F. under a nitrogen sweep to remove the condensed water from the reaction. The polyamines can comprise, for example, ethylenediamine, diethylenetriamine, triethylene tetraamine, amino ethyl piperazine and the like.

The polyamides can be converted to quaternary compounds by reaction with methylene chloride, dimethyl sulfate, benzylchloride, diethyl sulfate and the like. Typically the quaternization reaction would be effected at a

temperature of from about 100 to about 200° F. over a period of from about 4 to 6 hours.

The quaternization reaction may be employed to improve the chemical compatibility of the tackifying compound with the other chemicals utilized in the treatment fluids. Quaternization of the tackifying compound can reduce effects upon breakers in the fluids and reduce or minimize the buffer effects of the compounds when present in various fluids.

Additional compounds which may be utilized as tackifying compounds include liquids and solutions of, for example, polyesters, polyethers and polycarbonates, polycarbonates, styrene-butadiene lattices, natural or synthetic resins such as shellac and the like.

The tackifying compound is admixed with the particulate and the treatment chemical particles in an amount of from about 0.1 to about 3.0 percent active material by weight of the coated particulate. It is to be understood that larger quantities may be used, however, the larger quantities generally do not significantly increase performance and could undesirably reduce the permeability of the particulate pack. Preferably, the tackifying compound is admixed with the particulate and treatment chemical particles introduced into the subterranean formation in an amount of from about 0.25 to about 2.0 percent by weight of the coated particulate.

When the tackifying compound is utilized with another material that is to be admixed with the particulate and which is to be at least partially coated with the tackifying compound, such as glass fibers or the like, the compound is present in an amount of from about 10 to about 250 percent active material by weight of the glass fibers or other added material and generally from about 0.1 to about 3 percent active material by weight of the quantity of particulate with which the coated material is intimately admixed. Preferably the tackifying compound is present in an amount of from about 50 to about 150 percent of the material which is to be at least partially coated with the tackifying compound and then added to the particulate. At least a portion of the tackifying compound introduced with the additional material will contact and coat at least a portion of the particulate with which it is admixed.

The hardenable resin, when present, comprises an epoxy or phenolic resin or other compound capable of being at least partially coated upon a particulate substrate and then cured to a higher degree of polymerization. Examples of such resins include phenol-aldehyde resins of both the resole and novolac type, urea-aldehyde resins, melamine-aldehyde resins, epoxy resins, furfuryl alcohol resins and the like. The curing may result from heating the resin to a higher temperature such as can occur with the resole resins or by the addition of a catalyst or crosslinker to the resin which initiates polymerization. Admixtures of resins such as the resole and novolac resins may be utilized wherein sufficient novolac resin is incorporated to initiate polymerization in the novolac resin. Various resins are described in for example U.S. Pat. Nos. 5,420,174; 5,218,038; 5,425,994 and 4,888,240 the entire disclosures of which are incorporated herein by reference thereto. Particularly preferred resins include epoxy resins such as "EPON 828" epoxy resin from Shell Chemical Company, Houston, Tex. Phenolic resins such as "Resin 1866" from Acme Resin Corporation, Borden Division, Forrest Park, Ill., furan resins such as "ARS-1500" resin from Advanced Resin Systems, Des Plaines, Ill. and novolac Resins such as "Bakelite 9282 FPP" resin also available from Advanced Resin Systems.

The resin is admixed with the particulate in an amount of from about 0.01 to about 5.0 percent by weight of the

particulate. Preferably, the resin is admixed with the particulate in an amount of from about 0.05 about 1.0 percent by weight of the particulate. Curing agents, catalysts or crosslinkers selected from those well known in the art may be utilized with the resin to harden the resin and form a consolidated matrix of particulate.

The liquid or solution of tackifying compound interacts mechanically with the particles of particulate introduced into the subterranean formation to limit or prevent the flowback of particulates to the wellbore during initial flowback. When the hardenable resin is present, the tackifying compound substantially limits flowback prior to hardening and consolidation of the particulates by the hardenable resin. The tackifying compound causes the treatment chemical particles admixed with the coated particulates to adhere to the coated particles and to remain uniformly dispersed within the portion of the coated particulate to which it is added.

In one embodiment, the tackifying compound, when comprised of polyamides that contain reactive sites such as amine groups, may be admixed and contacted with a material that has multi-functional reactive sites which are capable of reacting with the reactive sites on the tackifying compound to form a hard reaction product which consolidates the agglomerates formed by the tackifying compound. A "hard reaction product" as used herein means that the reaction of the tackifying compound with the multifunctional material will result in a substantially nonflowable reaction product that exhibits a higher compressive strength in a consolidated agglomerate than the tackifying compound alone with the particulates. One means of evaluating the consolidated agglomerate to determine whether an increase in compressive strength has occurred is through testing with a penetrometer. Samples may be prepared comprising particulate coated with the tackifying compound, multifunctional material and an admixture as described herein and penetrometer readings can be made using equipment such as a PWG Penetrometer from Precision Scientific Company, Chicago, Ill. Comparison of the penetrometer readings readily demonstrates the change that has occurred as a result of the reaction. In this instance, the tackifying compound also functions as the hardenable resin. The material having multi-functional reactive sites include compounds such as aldehydes such as formaldehyde, dialdehydes such as glutaraldehyde, hemiacetals or aldehyde releasing compounds, diacid halides, dihalides such as dichlorides and dibromides, polyacid anhydrides such as citric acid anhydride, epoxides and the like. Preferred compounds for use with polyamides containing reactive sites comprise furfuraldehyde, glutaraldehyde or aldehyde condensates and the like. The multi-functional compound is admixed with the tackifying compound in an amount of from about 0.01 to about 50 percent by weight of the tackifying compound to effect formation of the reaction product. Preferably, the compound is present in an amount of from about 0.5 to about 1 percent by weight of the tackifying compound.

The liquid or solution of tackifying compound and hardenable resin generally are incorporated with the particulate in any of the conventional fracturing or gravel packing fluids comprised of an aqueous fluid, an aqueous foam, a hydrocarbon fluid or an emulsion, a viscosifying agent and any of the various known breakers, buffers, surfactants, clay stabilizers or the like.

Generally the tackifying compound and hardenable resin may be incorporated into fluids having a pH in the range of from about 3 to about 12 for introduction into a subterranean formation. The compounds are useful in reducing particulate movement within the formation at temperatures from about

ambient to in excess of 300° F. It is to be understood that not every hardenable resin or tackifying compound will be useful over the entire pH or temperature range but every compound is useful over at least some portion of the range and individuals can readily determine the useful operating range for various products utilizing well known tests and without undue experimentation.

The liquid or solution of tackifying compound and the hardenable resin generally are incorporated with the particulate as a simultaneous mixture by introduction into the fracturing or gravel packing fluid along with the particulate. The treatment chemical may be introduced in a similar manner and may be at least partially coated by the tackifying compound or may adhere to the particulate which has been at least partially coated with the tackifying compound. Fracturing fluid slurries are introduced into the subterranean formation at a rate and pressure sufficient to create at least one fracture in the formation into which particulate then is introduced to prop the created fracture open to facilitate hydrocarbon production. Gravel packing treatments generally are performed at lower rates and pressures whereby the fluid can be introduced into a formation to create a controlled particle size pack surrounding a screen positioned in the wellbore where fracturing of the formation may or may not occur. The particulate pack surrounding the wellbore then functions to prevent fines or formation particulate migration into the wellbore with the production of hydrocarbons from the subterranean formation. The treatment chemical then is dissolved by the fluids present in the formation to provide the desired treatment. The dissolution may be effected with either the natural formation fluids or a fluid that may be introduced into the formation specifically to dissolve the treatment chemical.

The gravel packing treatment also may be performed without a screen in the wellbore. In such a screenless completion, the fluid generally is introduced into the wellbore to fill the perforations and wellbore to a level above the perforations and permitted to consolidate. The consolidated pack can then be drilled or reamed out to reopen the bore while providing a consolidated pack to screen fines and formation particulate from migrating into the wellbore. When the treatment chemical comprises a breaker, uniform dispersion within the particulate pack can result in better clean-up of viscosifying agents from the gravel pack and higher pack permeability and less formation damage from the filter cake.

The tackifying compound may be introduced into the fluid before, after or simultaneously with introduction of the particulate into the fluid. The liquid or solution may be incorporated with the entire quantity of particulate introduced into the subterranean formation or it may be introduced with only a portion of the particulate, such as in the final stages of the treatment to place the intimate mixture in the formation in the vicinity of the wellbore. For example, the tackifying compound may be added to only the final 20 to 30 percent of the particulate laden fluid introduced into the formation and the hardenable resin may be added to only the last 10 to 20 percent of the particulate laden fluid. In this instance, the intimate mixture will form a tail-in to the treatment which upon interaction within the formation with the particulate will cause the particles to bridge on the agglomerates formed therein and prevent movement of the particles into the wellbore with any produced fluids. The tackifying compound and hardenable resin may be introduced into the blender or into any flowline in which they will contact the material to be at least partially coated by the compounds. The compounds may be introduced with meter-

ing pumps or the like prior to entry of the treatment fluid into the subterranean formation. The treatment chemicals generally will be introduced into those portions of the particulate that are coated with the tackifying compound unless the treatment chemical is itself at least partially coated with the tackifying compound. In this instance, the treatment chemical may be introduced with any of the particulate introduced into the subterranean formation.

In an alternate embodiment, the particulate may be pre-mixed with either the tackifying compound or the hardenable resin prior to admixing with a treatment fluid and the other constituents for use in a subterranean formation. In some instances, resin precoated particulates may be utilized and the tackifying compound then would be added during performance of the subterranean formation treatment. Depending upon the type of resin coating employed, a catalyst then would be added to the treatment fluid or introduced in a flush fluid or the like.

Surprisingly, it has been found that use of the method of the present invention can produce high permeability tunnels extending from wellbore perforations back into proppant packed fractures created in the subterranean formation which then may be consolidated. Control of the flowback rate of the treatment or formation fluids from the wellbore can be used to provide a controlled erosion of the treated particulate immediately adjacent a perforation in the wellbore. The flowback rate is controlled so as to provide a level above the initial critical resuspension velocity of the tackifying compound but generally is maintained below the continuous critical resuspension velocity. This results in controlled production of particulate from the formation. The erosion surprisingly has been found to be very uniform in nature and to create a tunnel into the particulate in the formation generally corresponding to the size and shape of the perforation in the wellbore. After the tunnel is formed, the hardenable resin consolidates the remaining particulate to provide a high permeability passage or tunnel from the formation to the wellbore.

To further illustrate the present invention and not by way of limitation, the following examples are provided.

EXAMPLE I

The evaluation of a liquid or solution of a compound for use as a tackifying compound is accomplished by the following test. A critical resuspension velocity is first determined for the material upon which the tackifying compound is to be coated. The apparatus comprises a $\frac{1}{2}$ " glass tee which is connected to an inlet source of water and an outlet disposal line is blocked to fluid flow. A water slurry of particulate is aspirated into the tee through the inlet and collected within a lower portion of said tee by filtration against a screen. When the lower portion of the tee is full, the vacuum source is removed and a plug is used to seal the end of the lower portion of the tee. The flow channel from inlet to outlet then is swabbed clean and a volumetrically controlled pump, such as a "MOYNO" pump, is connected to the inlet and a controlled flow of water is initiated. The velocity of the fluid is slowly increased through the inlet until the first particle of particulate material is picked up by the flowing water stream. This determines the baseline for the starting of the resuspension velocity. The flow rate then is further increased until the removal of particles becomes continuous. This determines the baseline for the continuous resuspension velocity. The test then is terminated and the apparatus is refilled with particulate having a coating corresponding to about 0.5 percent active material by weight of

the particulate applied thereto. Similar trends generally are seen in the results when the concentrations tested are from about 0.1 to about 3 percent, however, the 0.5 percent level which is within the preferred application range is preferred for standardization of the procedure. The test is repeated to determine the starting point of particulate removal and the velocity at which removal becomes continuous. The percent of velocity increase (or decrease) then is determined based upon the initial or continuous baseline value. The results of several tests employing the preferred polyamide of the present invention, and conventional epoxy and phenolic resins known for use in consolidation treatments in subterranean formations with 12/20 and 20/40 mesh sand are set forth below in Table I.

TABLE I

Test No.	Particulate Size	Coating Agent, % V/W Particulate	Percent of Velocity Change At:	
			Starting of Sand Particle Transport	Continuous Sand Transport
1	20/40 mesh sand	None	0	
2	20/40 mesh sand	$\frac{1}{2}$ percent polyamide	192	222
3	20/40 mesh sand	1 percent polyamide	271	391
4	20/40 mesh sand	$\frac{1}{2}$ percent phenolic	-0.5	6.5
5	20/40 mesh sand	1 percent phenolic	-9	-6.8
6	20/40 mesh sand	$\frac{1}{2}$ percent epoxy	-9	-1.2
7	20/40 mesh sand	1 percent epoxy	5.2	12.2
8	12/20 mesh sand	$\frac{1}{2}$ percent polyamide	228	173
9	12/20 mesh sand	1 percent polyamide	367	242
10	12/20 mesh sand	$\frac{1}{2}$ percent phenolic	42	22
11	12/20 mesh sand	1 percent phenolic	42	13
12	12/20 mesh sand	$\frac{1}{2}$ percent epoxy	48	30
13	12/20 mesh sand	1 percent epoxy	38	15

The data clearly illustrates the substantial increase in the critical resuspension velocity of a particulate coated with the tackifying compound in comparison to other known formation consolidation agents which require hardening to be effective.

The test results clearly demonstrate the beneficial results achieved by practice of the method of the present invention with respect to proppant production from a simulated formation.

EXAMPLE II

The stabilization properties of the method of the present invention are determined by comparison to untreated sand and sand including a tackifying compound. The flowback velocity is measured in an American Petroleum Institute approved simulated fracture flow cell. The cell contains Ohio sandstone cores having a proppant bed size of about 1.5 inches in height, about 7 inches in length and about 0.25 inches in width between the cores. The bed is initially prepacked with 20/40 mesh sand by introducing the sand into the cell in an aqueous slurry or a gelled fluid containing 40 pounds of guar per 1000 gallons of aqueous fluid. The

cell is fitted with a 0.3 inch hole at one end to simulate a perforation. The hole is visible through a sight glass so that proppant production through the hole can be visually determined.

The cell then was cleaned and packed with another proppant pack for testing. The tested materials are set forth in Table II, below.

TABLE II

SAMPLE	PACKING FLUID	ADDITIVES TO SAND, % BY WT.	FLOW RATE, ml/min AT WHICH FAILURE OCCURS
1	water	None	84
2	gel	None	90
3	gel	1% by wt polyamide	180
4	gel	2% by wt polyamide	384
5	gel	1% by wt polyamide and 1% out Bakelite 9282 FP resin	>3000 ¹
6	gel	1% by wt polyamide and 1% by wt Bakelite 9282 FP resin	>2600 ²

¹pack heated at 250° F. for 72 hours before testing, no sand production during test

²pack heated at 180° F. for 4 hours before testing no sand production during test

EXAMPLE III

The controlled release properties of the method of the present invention are determined by comparison to breaker solutions, untreated substrates containing breakers and substrates containing breaker including a tackifying compound.

The breaker utilized comprised sodium persulfate. The solution was prepared by dissolving 3 grams of sodium persulfate in 100 ml of deionized water. The particular substrates utilized comprised diatomaceous earth and amorphous silica. The diatomaceous earth substrate was prepared by dissolving 5 grams of sodium persulfate in 10 ml of deionized water to which was added 10 grams of diatomaceous earth. The sample then was dried for 24 hours in a 140° F. vacuum oven. The sample material has a concentration of 0.5 gram sodium persulfate per gram of diatomaceous earth. The amorphous silica substrate was prepared by dissolving 5 grams of sodium persulfate in 10 ml of deionized water to which was added 5 grams of amorphous silica. The sample then is dried for 24 hours in a 140° F. vacuum oven. The sample material has a concentration of 1 gram sodium persulfate per gram of amorphous silica.

The samples are admixed with a quantity of a crosslinked hydroxypropylguar containing fluid. The gelled fluid is prepared by hydrating hydroxypropylguar in tap water in an amount of 25 pounds per 1000 gallons of fluid. A liquid borate containing crosslinker such as described in U.S. Pat. No. 5,827,804 issued Oct. 27, 1998, the entire disclosure of which is incorporated herein by reference, then was admixed with the gelled fluid in an amount of 2 gallons per 1000 gallons of fluid. The crosslinked fluid then is admixed with a quantity of 20–40 mesh sand, tackifying compound and breaker or substrate loaded breaker in a concentration of 2 lbs. sodium persulfate per 1000 gallons of fluid. The tackifying compound was admixed with the sand and substrate prior to admixture with the crosslinked gel resulting in a partial coating of the substrate with the tackifying compound. The tackifying compound is present in an amount of

1.2 percent by weight of the sand present. Each sample is placed in a beaker and heated to 150° F. in a hot water bath. At designated intervals, the viscosity is measured on a Model 35 FANN™ Viscometer. The results of the tests are set forth in the Table III, below.

TABLE III

Sample	Breaker	pH	Tackifying Compound Present	Viscosity, cp			
				0.5 hr	1 hr	2 hr	3.5 hr
1	LS	8.47	No	C	C	1.5	1
2	LS	8.40	Yes	C	C	5	2.5
3	DE	8.45	No	C	C	1.5	1
4	AS	8.47	No	C	C	3	1.5
5	DE	8.48	Yes	C	C	9	3
6	AS	8.43	Yes	C	C	80	5

LS: liquid breaker solution

DE: diatomaceous earth substrate with breaker

AS: amorphous silica substrate with breaker

C: fully crosslinked fluid

The results clearly demonstrate the tackifying compound delayed the release of the breaker from the substrate material.

While the present invention has been described with regard to that which is currently considered to comprise the preferred embodiments of the invention, other embodiments have been suggested and still other embodiments will occur to those individuals skilled in the art upon receiving the foregoing specification. It is intended that all such embodiments shall be included within the scope of the present invention as defined by the claims appended hereto.

What is claimed is:

1. A method of introducing treatment chemicals and treating a subterranean formation comprising the steps of: introducing a particulate-containing fluid suspension into a subterranean formation;

admixing with at least a portion of said particulate in said fluid suspension a liquid or solution of a non-hardening tackifying compound whereby at least a portion of said particulate is at least partially coated by said compound;

admixing with at least a portion of said particulate in said fluid suspension a treatment chemical whereby at least a portion of said treatment chemical is contacted by said tackifying compound and at least partially coated therewith whereby the tackifying compound retards release of said treatment chemical in said fluid suspension; and

depositing the tackifying compound coated particulates and treatment chemical in the subterranean formation whereby upon flowing back fluid from the formation the tackifying compound coated treatment chemical is subsequently released within the subterranean formation to treat at least a portion of the formation or fluids in contact therewith.

2. The method of claim 1 wherein said tackifying compound comprises at least one member selected from the group consisting of polyamides, polyesters, polyethers, polycarbonates, polycarbonates, styrene-butadiene lattices and natural and synthetic resins.

3. A method of treating a subterranean formation comprising the steps of:

introducing a treatment fluid into a subterranean formation;

admixing with at least a portion of said fluid, a particulate which is introduced into and deposited within said fracture;

admixing with at least a portion of said particulate a liquid or solution of a tackifying compound comprising a polyamide whereby at least a portion of said particulate is at least partially coated by said compound such that the critical resuspension velocity of said at least partially coated particulate is increased by at least about 30 percent when tested at a level of 0.5% active material by weight over said particulate alone with water;

admixing with at least a portion of said particulate in said treatment fluid a treatment chemical whereby at least a portion of said treatment chemical is contacted by said tackifying compound and at least partially coated therewith whereby the tackifying compound retards release of said treatment chemical in said treatment fluid; and depositing the tackifying compound coated particulates and the treatment chemical in the subterranean formation whereby upon flowing back fluid from the formation the tackifying compound coated treatment chemical is subsequently released within the subterranean formation to treat at least a portion of the formation or fluids in contact therewith.

4. The method of claim 3 wherein said tackifying compound is admixed with said particulate in an amount of from about 0.1 to about 3.0 percent by weight of said particulate.

5. The method of claim 3 wherein said tackifying compound is admixed with said particulate in an amount of from about 0.25 to about 2 percent by weight of said particulate.

6. The method of claim 3 wherein said coated particulate has a critical resuspension velocity in excess of 100 percent over said particulate alone.

7. The method of claim 3 wherein said polyamide comprises predominately a condensation reaction product of a dimer acid containing some trimer and higher oligomers and some monomer acids with a polyamine.

8. The method of claim 7 wherein said treatment chemical comprises at least one member selected from the group consisting of scale inhibitors, biocides, breakers, buffers, paraffin inhibitor and corrosion inhibitors.

9. The method of claim 8 wherein said treatment chemical is coated upon or absorbed upon an inert porous substrate or a non-porous substrate.

10. A method of treating a subterranean formation penetrated by a wellbore comprising the steps of:

providing a fluid suspension including a mixture of a particulate material and another material comprising a treatment chemical which are at least partially coated with a liquid or solution of a non-hardening tackifying compound;

introducing the fluid suspension into a subterranean formation through a wellbore; and

depositing the fluid suspension in the formation whereupon flowing back fluid from the formation the tackifying compound retards movement of at least a portion

of the particulate material from the formation into the wellbore and retards release of the treatment chemical within the fluid within at least a portion of the said formation.

11. The method of claim 10 wherein said treatment chemical comprises at least one member selected from the group consisting of scale inhibitors, biocides, breakers, buffers, paraffin inhibitor and corrosion inhibitors.

12. The method of claim 10 wherein said treatment chemical is coated upon or absorbed upon an inert porous substrate or a non-porous substrate.

13. The method of claim 10 wherein said tackifying compound is present in an amount of from about 0.1 to about 3% by weight of said particulate.

14. The method of claim 10 wherein said tackifying compound comprises at least one member selected from the group consisting of polyamides, polyesters, polyethers, polycarbonates, polycarbonates, styrene-butadiene lattices and natural and synthetic resins.

15. A method of treating a subterranean formation penetrated by a wellbore and controlling fines migration in a particulate pack placed within said formation comprising the steps of:

providing a fluid suspension including a mixture of a particulate material and another material comprising a treatment chemical which are at least partially coated with a liquid or solution of a tackifying compound; introducing the fluid suspension into a subterranean formation through a wellbore; and

depositing the fluid suspension in the formation whereupon flowing back fluid from the formation the tackifying compound coated particulate retards movement of at least a portion of any fine particulate material moving to said wellbore from the formation and the tackifying compound coated upon said treatment chemical retards release of the treatment chemical within at least a portion of said formation.

16. The method of claim 15 wherein said treatment chemical comprises at least one member selected from the group consisting of scale inhibitors, biocides, breakers, buffers, paraffin inhibitor and corrosion inhibitors.

17. The method of claim 16 wherein said treatment chemical is coated upon or absorbed upon an inert porous substrate or a non-porous substrate.

18. The method of claim 15 wherein said tackifying compound is present in an amount of from about 0.1 to about 3% by weight of said particulate.

19. The method of claim 15 wherein said tackifying compound comprises at least one member selected from the group consisting of polyamides, polyesters, polyethers, polycarbonates, polycarbonates, styrene-butadiene lattices and natural and synthetic resins.

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(12) **United States Patent**
Wang et al.

(10) Patent No.: **US 6,458,867 B1**
(45) Date of Patent: **Oct. 1, 2002**

- (54) **HYDROPHILIC LUBRICANT COATINGS FOR MEDICAL DEVICES**
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- (73) Assignee: SciMed Life Systems, Inc., Maple Grove, MN (US)
- (*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.
- (21) Appl. No.: 09/406,987
- (22) Filed: Sep. 28, 1999
- (51) Int. Cl.⁷ A01N 1/00
- (52) U.S. Cl. 523/105; 523/112; 523/113; 604/265; 606/108; 623/1.11
- (58) Field of Search 604/265; 606/108; 623/1.11; 523/105, 112, 113

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(74) *Attorney, Agent, or Firm*—Vidas, Arrett & Steinkraus P.A.

(57) **ABSTRACT**

The present invention relates to a medical device comprising at least one tubular member having an inner surface and an outer surface. The inner surface of the tubular member is at least occasionally subjected to contact with at least one second surface. The tubular member therefore comprises a hydrophilic lubricious coating disposed on its inner surface to reduce the friction between the inner surface of the tubular member and the second surface which is caused by movement.

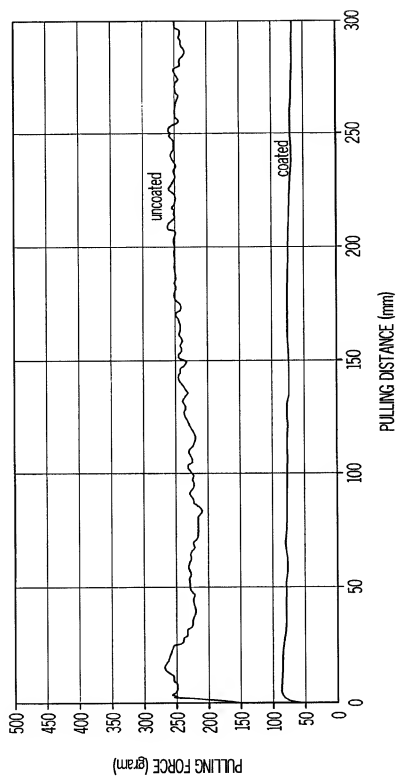


FIG. 1

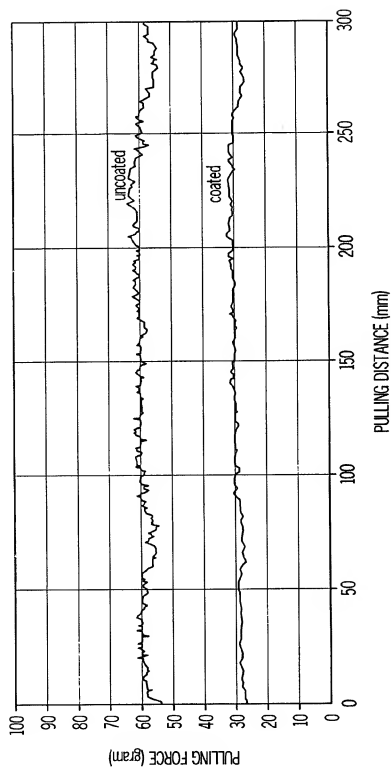


FIG. 2

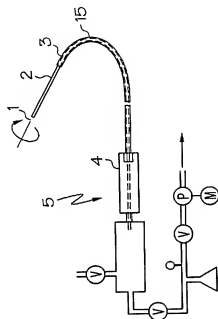


FIG. 5

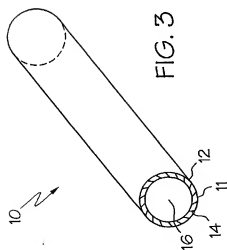


FIG. 3

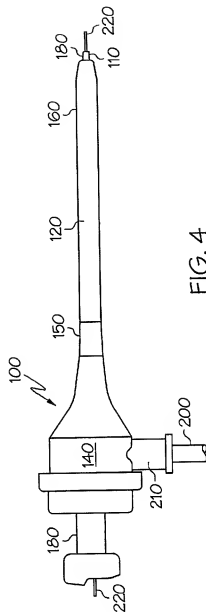


FIG. 4

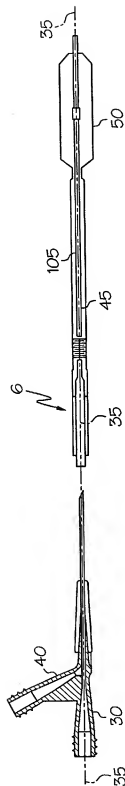


FIG. 6

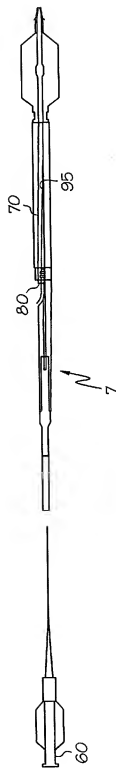


FIG. 7

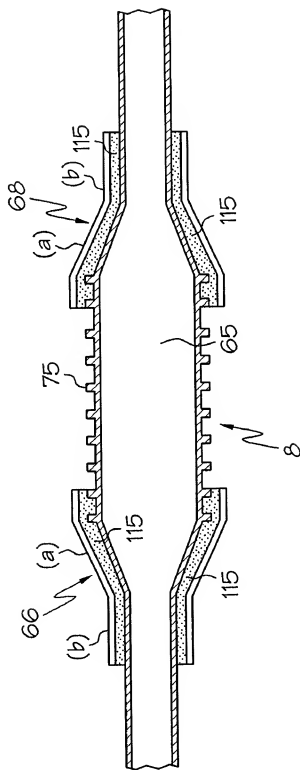


FIG. 10

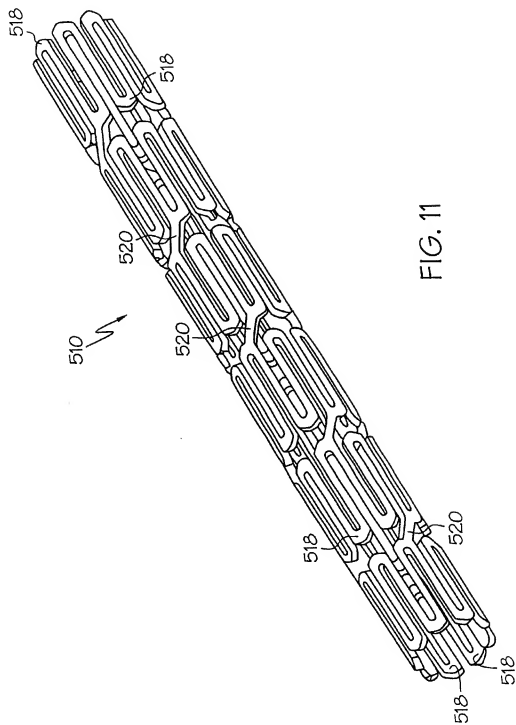


FIG. 11

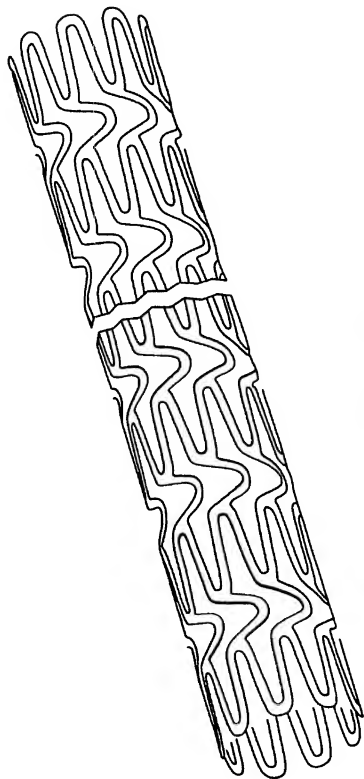


FIG. 12

HYDROPHILIC LUBRICANT COATINGS FOR MEDICAL DEVICES

FIELD OF THE INVENTION

This invention relates to a water soluble lubricious coating for a medical device such as a catheter assembly.

BACKGROUND OF THE INVENTION

Catheters are used in surgical procedures for insertion into blood vessels, urethra, or body conduits during such procedures as coronary angioplasty, stent delivery and placement for the opening of occluded or blocked blood vessels, for urological and reproductive surgeries, and to deliver biologically compatible fluids, such as radiologically opaque fluid for contrast x-rays to precise locations within the body.

Depending on the procedure involved, catheters may be one of several different types including an over the wire, a single operator exchange or a fixed wire catheter assembly.

Over the wire catheters may be used as guide catheters during coronary angioplasty, for instance. The guide catheter provides access to the area in which the stenosis or blockage may be found, and provides support for the treatment catheter which often includes a balloon dilatation system wherein a dilatation balloon is delivered to a site of stenosis in an artery and is used to alleviate the stenosis.

In operation, the guide catheter is introduced over a guide wire through a previously placed introducer sheath and advanced through a blood vessel to the location of a stenosis. The guide wire can then be removed.

Other procedures may involve the introduction of other medical devices at precisely specific bodily locations including the delivery of stents, stent-grafts, grafts, vena cava filters, other expandable medical devices, and so forth.

During these procedures, the catheters must be able to traverse tortuous pathways through blood vessels to the stenosis in a manner as atraumatic to the patient as possible. It is therefore desirable to make insertion through the patient in such a way to limit the insertion time and discomfort as much as possible.

A common problem which occurs in catheter assemblies is friction or adhesion between various parts which periodically come into contact with one another during the medical procedure. For instance, friction can occur between the guide catheter and guide wire, between the introducer sheath and the guide catheter, or between the guide catheter and the balloon catheter, for instance, and may increase the difficulty of insertion, cause loss of catheter placement, and result in discomfort or damage to the patient. It is therefore desirable to improve the moving relationship between the various parts of the catheter assemblies.

The materials from which catheters are produced are typically polymeric or metallic in nature, and in general, are inherently non-lubricious. When these non-lubricious materials come into contact, friction occurs. Medical device manufacturers have used various approaches to reduce the coefficient of friction between these surfaces.

Hydrophobic coatings have been used to impart lubricity to medical devices including silicone based lubricants, glycerine or olive oil. These coatings have been known to wash off when exposed to an aqueous environment, lose initial lubricity rapidly, and lack abrasion resistance. Residual amounts of silicone have also been known to cause tissue reaction and irritation in patients. The loss of lubricity can lead to discomfort during insertion into a patient, and

damage to blood vessels and tissues due to frictional forces during insertion or removal of the device. Examples of silicone based lubricants include polysiloxanes and modified polysiloxanes. Often they include a polar group which may be an aminoalkyl or carboxyalkyl terminating group. U.S. Pat. No. 5,084,315 to Karimi et al. issued Jan. 28, 1992 discusses the problems with migration and bleeding.

U.S. Pat. No. 5,266,359 to Spielvogel issued Nov. 30, 1993 describes a lubricating composition for a medical device which includes an emulsion of a noncuring polysiloxane, a surfactant and water. The surfactants are copolymers of polysiloxane and polyoxyethylene which are reactive and when cured, adhere to the surface. While Spielvogel teaches a method of application which does not utilize solvent, the problems associated with silicone based lubricants remain.

U.S. Pat. No. 5,272,012 to Opolski issued Dec. 21, 1993 describes a method for providing a medical apparatus with a protective lubricious coating comprising providing a coating solution which contains a protective compound such as a urethane, a slip additive such as a siloxane, and optionally, a crosslinking agent for the protective compound such as polyfunctional aziridine, coating the solution onto a surface of a medical apparatus and allowing the coating to set. The protective compound binds the slip additive such that domains of the slip additive are exposed in the formed layer. The coating solution may also contain a crosslinking agent. The protective compound binds the slip additive such that domains of the slip additive are exposed in the formed layer. The coating solution may also contain a crosslinking agent. The protective compound preferably has functional moieties capable of crosslinking to other moieties within the protective compound and with moieties derived from the medical device.

Another approach for reducing the coefficient of friction is to add a layer of a low friction material such as polytetrafluoroethylene, hereinafter PTFE and commonly known by the trademark of Teflon®. For instance, PTFE may be added as an inner layer of an internal catheter lumen to reduce friction between the guide catheter and the treatment catheter, for instance. The problem with the use of this inner layer of PTFE is that it requires a separate extrusion process, and also requires etching. Adhesion is also generally a problem between the PTFE and the polymeric catheter material as well. U.S. Pat. No. 5,647,846 to Berg et al. solved these problems through the use of a geometrically configured inner surface of the inner layer of a guide catheter, achieving low friction properties through geometry, rather than through the use of a lubricious polymer, thereby eliminating the need for the lubricious polymer. Berg et al. however, discusses forming the inner layer of a lubricious polymer, such as PTFE, or alternatively, coating the inner surface with a lubricant such as silicone.

Hydrophilic compounds have also been used to impart lubricity in medical devices. Such compounds are biocompatible or blood compatible, and are more readily discharged from the body and have less of a tendency to cause tissue irritation. However, because of the hydrophilicity, it is also more difficult to retain such coatings on the surface of the medical device throughout the procedure. U.S. Pat. No. 5,509,899 to Fan et al. issued Apr. 23, 1996 describes a lubricious coating for a medical balloon and catheter wherein the balloon is tightly wrapped and folded upon itself tortuously and tightly so that when in contact with each other for insertion into the body, the balloon is free of bridging and adhesion between abutting surfaces. The balloon has a base of a continuous polymeric surface which is expandable from

a folded, wrapped configuration with surfaces touching each other. Examples of such polymeric materials include Nylon, Sellar®, polyethylene terephthalate, polyethylene or similar materials. These materials may provide excellent balloon stock but are not necessarily sufficiently lubricious to be used by themselves. Therefore, a lubricious, biocompatible hydrogel coating is disposed on the polymeric surface and a thin, lubricious, blood-compatible coating is disposed upon the hydrogel coating and adheres to it to prevent abutting surfaces of folded polymer surfaces from adhering to each other during inflation and also to prevent delamination of the hydrogel coating and/or rupture of the balloon. The blood-compatible coating is polyethylene glycol, methoxy polyethylene glycol or mixtures thereof having a molecular weight between about 100 and 20,000 grams per mole.

U.S. Pat. No. 5,849,368 to Hostettler et al. issued Dec. 15, 1998 describes a process for rendering the surfaces of polymeric plastic or rubber materials, which are intrinsically non-polar or only slightly polar, polar or more polar, and hydrophilic, so that amine-containing functional groups, and ultimately, a durable tenaciously adhering, slippery polyurethane or polyurethane-urea hydrogel coating may subsequently be applied to the polymer surface. The process involves dual plasma-treatment of a polymeric plastic or rubber substrate material such that amine and amino groups are affixed to the substrate surface to make it more hydrophilic and reactive toward the terminal isocyanate groups of the polyurethane or polyurethane-urea prepolymer.

Although each of these methods describes a way in which the coefficient of friction may be reduced, a need still exists for a simple, easy to apply coating which is lubricious and biocompatible, and which has good retention on the surface of the device.

The present inventors have found a hydrophilic lubricant coating for medical devices, and in particular for catheter assemblies, to render inherently non-lubricious surfaces, lubricious, and a method for coating such devices which involves coating the inner surface a tubular member of a medical device. This hydrophilic lubricant coating overcomes the aforementioned problems associated with conventional lubricious coatings, and the problems associated with the use of silicone based lubricants and the addition of polytetrafluoroethylene layers.

SUMMARY OF THE INVENTION

This invention relates to a coating for rendering a medical device lubricious. The coating comprises pretreating primer composition, and a hydrophilic lubricious coating. The primer composition comprises substituents that are capable of adhering or bonding to, and improving the retention of the hydrophilic lubricious to the surface of the medical device. One such mechanism through which the primer compound may retain the hydrophilic polymer, is through hydrogen bonding.

This invention further relates to a medical device comprising at least one tubular member having an inner surface and an outer surface. The inner surface of the tubular member is at least occasionally subjected to contact with at least one second surface. The tubular member further comprises a hydrophilic coating disposed on the inner surface. The hydrophilic coating is present to inhibit the inner surface of the tubular member and the second surface from adhering to each other, and reduces the friction caused by movement between the two surfaces. The inner surface may first be pretreated with the primer composition.

The tubular member preferably comprises at least one thermoplastic polymer and the second surface preferably comprises a metal.

The hydrophilic coating may be coated on the inner surface of the tube by injection, or coextrusion.

This invention further relates to a catheter assembly comprising at least one polymeric sheath having an inner surface and an outer surface. The inner surface of the first polymeric sheath is at least occasionally subjected to contact with at least one second surface, and comprises a water soluble coating disposed on the inner surface of the polymeric sheath. The hydrophilic coating is present to inhibit the inner surface and the second surface from adhering to each other.

The polymeric sheath comprises at least one thermoplastic polymeric material. The second surface to which the inner surface of the polymeric sheath comes into contact may be a polymeric material or a metal.

The inner surface of the polymeric sheath may first be coated with a primer of a crosslinkable composition which is readily wettable. This improves the uniformity and shelf stability of the lubricious coating. The water soluble lubricious coating may further comprise Vitamin E to further improve the shelf stability of the coating.

The present invention further relates to a stent deployment catheter assembly having at least one tubular member for retention and release of a stent. The tubular member may be a retractable sheath, or it may be at least one stent retaining sleeve. A hydrophilic lubricious coating is disposed on the inner surface of the tubular member in order to facilitate stent release by reducing the coefficient of friction between the tubular member and the stent.

The lubricious coating of the present invention provides improved lubricity, eliminates migration problems associated with oil based lubricants and eliminates tissue reaction and irritation associated with oil based silicone lubricants.

Furthermore, due to the excellent lubricity, the diameter of the outer sheath of a medical device may be decreased thereby improving performance.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates the reduction in the wire movement frictional force achieved for Example 1 using the lubricious coating method of the present invention.

FIG. 2 illustrates the reduction in the wire movement frictional force achieved for Example 2 using the lubricious coating method of the present invention.

FIG. 3 shows generally a tubular member having coated on its inner surface, the hydrophilic coating of the present invention.

FIG. 4 shows a side view of a catheter sheath introducer having a hydrophilic coating on the inner surface of the tubular sheath of the catheter sheath introducer.

FIG. 5 shows a side view of a medical device used for passing a high-rotational-speed cutting tool into a vessel to remove abnormal deposits having the hydrophilic lubricious coating of the present invention disposed on the inner surface of guiding catheter.

FIG. 6 shows a side view of an over-the-wire catheter device specifically designed as a dilatation catheter for an inflatable balloon having the lubricious coating of the present invention disposed on the inner surface of the guide wire lumen.

FIG. 7 shows a rapid exchange embodiment of a balloon catheter device which is similar in construction to the catheter device shown in FIG. 6.

FIG. 8 shows a side view of a stent delivery catheter utilizing an inflatable balloon for releasing the stent. The

lubricious coating of the present invention is disposed on the inner surface of the stent retaining sleeves.

FIG. 9 shows a side view of a different embodiment of a stent delivery catheter with a loaded stent in the fully deployed position. This particular stent delivery catheter has retractable sheaths.

FIG. 10 shows a side view of a rapid exchange embodiment of a stent very similar in configuration to that shown in FIG. 9.

FIG. 11 illustrates a tubular, flexible, self-expanding stent shown in its unexpanded state.

FIG. 12 illustrates a tubular, flexible, balloon-expandable stent shown in its unexpanded state.

DETAILED DESCRIPTIONS OF THE PREFERRED EMBODIMENTS

FIG. 3 illustrates generally at (10) a tubular member which may be utilized in a medical device. The tubular member comprises an outer surface (12), and an inner surface (14), the inner surface forming a lumen (16). The lumen may be, for instance, a guide wire lumen for a catheter which is used in surgical procedures such as coronary angioplasty, stent delivery and placement for the opening of occluded or blocked blood vessels, for urological and reproductive surgeries, and to deliver biologically compatible fluids, such as radiologically opaque fluid for contrast x-rays to precise locations within the body.

A water soluble lubricious coating (11) is disposed on the inner surface (14) of the tubular member (10). The coating reduces the coefficient of friction between the tubular member and any surface with which it comes into contact, and which are in a moving or sliding relationship with one another. The tubular member may be comprised of a polymeric material for instance, which is inherently non-lubricious. The tubular member may form any type of catheter including balloon catheters and stent delivery catheters, retractable sheaths or stent retaining sleeves for stent delivery catheters, guide wire lumens, pull wire lumens, and so forth.

FIG. 4 illustrates generally at 100 a catheter introducer having a tubular sheath (120) and a hub (140) attached to the proximal end (150) of tubular sheath (120). A branch conduit (200) and a locking sleeve (210) is provided to allow for, among other things, connections to saline solution or medicines and access to other medical procedures. A guide wire (220) is shown as it is often used with such devices as balloon angioplasty catheters. A dilator unit is shown at (180). Hydrophilic coating (110) is disposed on the inner surface of tubular sheath (120) for inserting and guiding a catheter into living tissue.

A core wire may first be inserted through a hollow needle which is placed through the skin into the lumen of the desired blood vessel. The catheter introducer which comprises the tubular sheath (120), and a removable hollow stylet or dilator unit (180) may be advanced together over the core wire into the vessel. The core wire and dilator unit are then removed, leaving only the tubular sheath (120) of the catheter introducer present in the vessel. A catheter may then be advanced through the tubular sheath (120), into an artery for conventional purposes of angioplasty or any other desired purpose.

The tubular sheath (120) may therefore come into contact with a core wire (220), dilator unit and catheter (180). The hydrophilic coating (110) on the inner surface of the tubular sheath (120) reduces the friction between the tubular sheath

and the medical apparatus with which it comes into contact. These tubular sheaths may be utilized to maneuver medical devices such as catheter delivery devices for dilatation balloons, stents, stent-grafts, grafts, vena-cava filters, or other such devices to the desired location.

Catheter sheath introducer (100) is typical of current, commercially available introducers but many modifications can be made. Proximal end (150) of sheath (120) may, for instance, be made of a rigid material while distal end (160) of sheath (120) may be made of flexible material for better control outside the body by the physician, for instance.

Introducer type devices are known in the art and there are a vast number of different embodiments of such devices for which the present invention would find utility. Introducer type devices are illustrated in U.S. Pat. No. 5,066,285 issued Nov. 19, 1991 to Hillstead and in U.S. Pat. No. 5,466,230 issued Nov. 14, 1995 to Davila incorporated by reference herein.

FIG. 5 illustrates generally at (5), one embodiment of a medical device used for passing a high-rotational-speed cutting tool into a vessel to remove abnormal deposits. The cutting tool (1) is mounted at the end of a flexible drive shaft which transmits torque from a torque-generating device (4), such as an electric or pneumatic motor. The drive shaft (2) is surrounded for most of its length by a guiding catheter.

Another embodiment in which the present invention may be utilized is in a surgical cutting device illustrated in U.S. Pat. No. 5,651,781 issued Jul. 29, 1997 to Grace, incorporated by reference herein. The outer sheath in Grace houses a surgical cutting apparatus including a hollow cylindrical cutting blade member. The blade may be extended and retracted.

In order to provide a low-friction passage of rotational motion between the drive shaft (2) and the guiding catheter (3), the inner surface of the guiding catheter (3) may be coated with the lubricious coating of the present invention (15). Such devices are described in detail in U.S. Pat. No. 4,445,509 issued May 1, 1984 and in U.S. Pat. No. 4,990,134 issued Feb. 5, 1991, both to Auth, herein incorporated by reference.

The coatings of the present invention may be incorporated into both over-the-wire (OTW) catheters and rapid-exchange (RX) or single operator catheters. These types of catheter construction are also used in stent deployment catheters.

FIG. 6 illustrates generally at (6) an over-the-wire catheter device specifically designed as a dilatation catheter for an inflatable balloon (50) which device comprises a manifold system designated generally at (30). The manifold (30) may further comprise a inflation luer (40). Guide wire (35) extends through the guide wire lumen (45) which is coated on the inner surface with the lubricious coating of the present invention (105), for reducing the wire movement frictional force, thereby improving the sliding relationship, between the guide wire (35) and the inner surface of the guide wire lumen (45). The guide wire lumen (45) encloses the guide wire (35), which aids in the navigation of the catheter (6) through the appropriate vessel.

FIG. 7 illustrates generally at (7) a rapid exchange embodiment of a balloon catheter device which is similar in construction to the catheter device shown in FIG. 6. The inner surface of the guide wire lumen (70), including the port (80) of the guide wire lumen, is coated with the lubricious coating of the present invention (95) to reduce wire movement friction when a guide wire is introduced into port (80), and is advanced through the guide wire lumen (70).

The coatings of the present invention may also be utilized in stent deployment catheter systems as well as in angioplasty balloon catheters. In the case of a stent deployment catheter system, balloons may be utilized to expand the stent once it is in position for deployment, or the stent may be self-expanding. Retractable sheaths may be utilized wherein the sheath is moved over the stent once it is in position. The retractable sheath may act both to protect the stent, as well as to prevent it from expanding prematurely. Once the sheath is retracted, the stent can expand. The coatings of the present invention may also be utilized as a coating on the inner surface of the retractable sheath, for instance.

Stent deployment catheter devices, including those having a retractable sheath, are described in U.S. Pat. No. 5,534,007 issued Jul. 9, 1996 to St. Germain et al., herein incorporated by reference.

FIG. 8 shows generally at (8) a sideview of a stent delivery catheter assembly. In this embodiment, catheter (8) has an expandable portion or balloon (65). Disposed about the balloon (65) is a stent (75). Stent (75) may be any type of stent capable of being delivered by a stent delivery catheter, and may be self-expanding, or may be balloon expandable. In this embodiment, the stent (75) is balloon expandable.

Attached to the catheter are a pair of stent retaining sleeves (66) and (68). The sleeves each include a first portion (a) and a second portion (b). When balloon (65) is in a non-inflated state, the first sleeve portions (a), overlay the ends of balloon (65) as well as the ends of stent (75), holding the stent in position. Regardless of the inflated or non-inflated state of balloon (65), the second sleeve portions (b), are fixedly attached to catheter (8). When balloon (65) is inflated, stent (75) releases from sleeve portions (66a) and (68a).

Stent retaining sleeves (66) and (68) may be formed of many different polymeric materials. These polymeric materials are typically inherently non-lubricious. Stent (75) is typically a metal such as a metal alloy of nickel and titanium. For reducing the coefficient of friction, and improving the sliding relationship between retaining sleeves (66) and (68), and stent (75), the lubricious coating of the present invention (115) is disposed on the inner surface of the pair of sleeves (66) and (68).

FIG. 9 shows generally at (400) a catheter delivery device having a self-expanding stent (335) in a fully deployed position. The device generally comprises a proximal outer (410) which is characterized by a flexible tube which contains a pull wire lumen and optionally a guide wire lumen (315). The outer (410) may be comprised of a polymeric material such as high density polyethylene (HDPE) or Surlyn®. Preferably, the guide wire lumen (315) encloses a guide wire (320) which aids in the navigation of the catheter (305) through the appropriate vessel. The guide wire lumen (315) may be made of a flexible, but incompressible construction such as a polymer encapsulated braid or coil. The lubricious coating (325) of the present invention may be disposed on inner surface of the guide wire lumen (315) to reduce the coefficient of friction between the guide wire (320) and the guide wire lumen (315).

This catheter delivery device has a distal sheath (340) which covers stent (335) when it is loaded. FIG. 9 illustrates distal sheath (340) in a fully retracted state and collapsible sheath (350) is in its compressed state thereby releasing the stent (335) to allow it to self-expand against the vessel wall (465). The hydrophilic coating (325) is disposed on the inner surface of the retractable sheath (340) to reduce the coefficient of friction between the retractable sheath (340) and the stent (335).

Further, the retractable distal sheath (340) which covers and contains the loaded stent (335), and holds the self-expanding stent (335) in its reduced delivery configuration, is connected to a retracting member (445). The retracting member (445) may be a rod, a cable, a tube which may also be used to transport fluids, a pull back wire, guide wire, or the like. The retracting member (445), e.g., a pull wire, extends longitudinally within the proximal outer (410), optionally through a retracting member lumen (not shown), such as an HDPE, nylon, or polyether block amide (Pebax®) tube. In a more specific embodiment, the retracting member lumen extends longitudinally through the proximal outer (410), and houses the pull back wire (445). The inner surface of the retracting member lumen may have disposed on its inner surface thereof, the lubricious coating of the present invention for reducing the coefficient of friction between the pull back wire (445) and the retracting member lumen.

FIG. 10 illustrates a rapid exchange embodiment of a catheter delivery device which is similar in construction to that found in FIG. 9.

FIG. 11 illustrates a tubular, flexible, self-expanding stent shown in FIG. 11 in an unexpanded state. The self-expanding stent shown in FIG. 11 may be used with either of the stent delivery catheters shown in FIG. 9 or FIG. 10. The retractable sheath (340) is pulled back with pull back wire (445) to release the stent. As shown in FIGS. 9 and 10, the lubricious coating (325) of the present invention (340) disposed on the inner surface of the retractable sheath (340) to reduce the coefficient of friction between the retractable sheath (340) and the stent for a smooth, easy release. These stents are described in detail in U.S. patent application Ser. No. 09/122,431 herein incorporated by reference.

FIG. 12 illustrates a balloon expandable stent which may be utilized with the balloon as shown in FIG. 8. As shown in FIG. 8, the lubricious coating of the present invention (115) is disposed on the inner surface of the pair of sleeves (66) and (68) to reduce the coefficient of friction between the stent retaining sleeves (66) and (68) and the stent for easier and smoother release of the stent. This type of stent is described in detail in U.S. Pat. No. 5,843,120, herein incorporated by reference.

Catheter devices such as those illustrated in FIG. 9 and FIG. 10 are explained more fully in detail in U.S. Pat. No. 5,534,007 to St. Germain et al. issued Jul. 9, 1996 and herein incorporated by reference.

In a preferred embodiment of the present invention, the hydrophilic lubricious coating (115) is a carboxylic acid, or alcohol, which has been converted from a nonhydrophilic polymeric material having, for instance, ester or amide groups capable of undergoing hydrolysis. Poly(maleic anhydride) may also be hydrolyzed to a carboxylic acid. In this embodiment, the polymeric material which forms the coating is coextruded simultaneously with the polymeric material used for forming sleeves (66) and (68). The sleeves may be formed from a variety of organic high polymer materials such as polyamide, polyester, polyvinyl chloride, polystyrene, polyacrylate, polymethacrylate, polyacrylonitrile, polyacrylamide, polyethylene, polypropylene, polyurethane, polyvinyl acetate, silicone resins, polytetrafluoroethylene (PTFE) and copolymers and blends thereof. The result is a two layered tubular construction wherein the inner layer is a hydrophobic polyester or polyamide, and the outer layer is a polymeric material which may be any material listed above, as well as many others.

The inner layer of hydrophobic polyester or polyamide is then hydrolyzed either through acid or base catalysis, to a

carboxylic acid, or alcohol. The result is a layer of hydrophilic lubricious coating. The sleeves are then cut from the tubular member resulting in a layered structure of hydrophilic coating on the inner surface and hydrophobic polymeric material on the outside.

The coatings of the present invention may be utilized to improve the deployment of any of stents, stent-grafts, grafts or vena cava filters, or other such expandable medical devices, by coating the inner surface of the polymeric sheath to reduce the friction between the sheath and the stent.

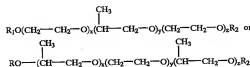
There are vast number of variations of catheter devices commercially available and the present inventors envision that the coating method described herein may be employed in any such device.

The devices discussed herein are meant only for illustration as to how the coatings of the present invention may be utilized, and are by no means intended as an exclusive list. One of skill in the art would understand how to incorporate the coatings and method of the present invention to any other such devices.

There are various types of hydrophilic polymers which may be useful to the present invention including both non-reactive and reactive. Hydrophilicity may also be obtained by the reaction of polymers in the presence of water which then subsequently form water soluble moieties. The hydrophilic lubricants useful herein include polyalkylene glycols, alkoxy polyalkylene glycols, copolymers of methyvinyl ether and maleic acid, poly(vinylpyrrolidone), poly(acrylamide) including poly(N-alkylacrylamide), poly(acrylic acid), poly(saccharide), poly(vinyl alcohol), poly(ethyleneimine), polyamides, methyl cellulose, dextran, modified dextran, chondroitin sulphate, lecithin, and so forth. The polymers are typically chain-structured, non-crosslinked and water soluble having a hydrophilic group such as $-\text{OH}$, $-\text{CONH}_2$, $-\text{COOH}$, $-\text{NH}_2$, $-\text{COO}-$, $-\text{SO}_3-$, $-\text{NR}_3^+$ and so forth where R is alkyl or hydrogen.

Derivatives of these polymers may also be utilized providing, even if they are not water soluble, that they are still of a structure which is capable of being hydrated, or is dispersible in water. Examples include esterified polymers, salts, amides, anhydrides, halides, ethers, hydrolyzates, acetals, formals, alkylols, quaternary polymers, diazo, hydrazides, sulfonates, nitrates, and ion complexes which are obtained by condensation, addition, substitution, oxidation, or reduction reactions of the above mentioned water soluble polymers. Also useful are polymers crosslinked with substances having more than one reactive functional group such as diazonium, azide isocyanate, acid chloride, acid anhydride, imino carbonate, amino, carboxyl, epoxy, hydroxyl and aldehyde groups. Further polymers include those copolymerized with vinyl, acrylic acid, methacrylic acid, diene compounds, and so forth.

A preferred class of hydrophilic lubricants are polyalkylene glycols or alkoxy polyalkylene glycols which have the following general formula:



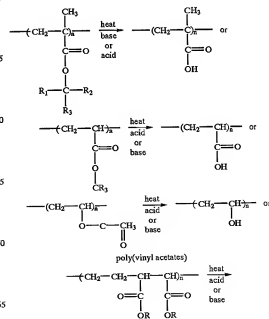
R1 and R2 may be the same or different and can be H or an alkyl group having 1 to about 6 carbon atoms; x is from 2 to about 500; and y is from 0 to about 100.

The polyalkylene glycols and alkoxy polyalkylene glycols may also contain functional groups such as, for example, hydroxyl, sulfur, nitrogen or oxygen.

In a more specific preferred embodiment of the present invention, the water soluble lubricants are copolymers of polyalkylene glycols or alkoxy polyalkylene glycols. Specific examples of such copolymers include Pluronic® 31R1 surfactant, a polyoxypropylene/polyoxyethylene block copolymer available from BASF Corp. in Mount Olive, N.J. and Cremophor® EL 35, an ethoxylated castor oil (PEG 35 Castor Oil) or polyoxyethylene/glycerol triricinolein available from BASF Corp. in Wyandotte, Mich.

Alternatively, the lubricious coatings can be formed from hydrophobic compounds which can be converted to a lubricious hydrophilic compound through a chemical reaction such as hydrolysis, for instance. The conversion may take place once the coating process is complete. Examples of such compounds include those compounds having pendant ester or amide groups, such as, for instance, esters such as poly(acrylates), poly(meth)acrylates, poly(vinyl esters), poly(maleates), poly(fumerates), polyamides, poly(acrylamides), and copolymers and terpolymers thereof, and so forth. The poly(acrylic), poly(methacrylic) or polymaleic esters, and the polyamides or poly(acrylamides) may be converted to carboxylic acids by hydrolysis. Hydrolysis may be basic or acidic, and heat may be added to increase the rate of reaction. Esters are hydrolyzed reversibly in the presence of acid or irreversibly in the presence of base. The use of a large excess of water in the acid-catalyzed reaction favors hydrolysis. Vinyl esters may also be converted to an alcohol through saponification using an alkali-metal hydroxide which forms the alcohol and the metal salt of the acid. While most of these materials are hydrophobic, some are hydrophilic and can be hydrolyzed as well.

The following reaction schemes illustrate this embodiment of the present invention:



typically a first tubular member or outer sheath which forms a lumen within which other tubular members or metal wires may be housed. The outer sheath is made up of a distal portion and a proximal portion. Typically, the tubular member will be a thermoplastic polymeric material which is capable of being molded into a shaped article such as a hollow tube. Such materials may include, but are not limited to, homopolymers, copolymers and terpolymers of ethylene; homopolymers, copolymers and terpolymers of propylene; polyesters; polyamides; polyurethanes; vinylic copolymers; block copolymers; and so forth. For instance, materials as Nylon, Sclaflo, polyether-polyester block copolymers (i.e. Hytrel®), Pebax®, Surlyn®, polyethylene terephthalate, polytetrafluoroethylene, polyvinyl chloride, polyurethanes, polyetherurethanes, polyesterurethanes, polyurethane ureas, polyurethane siloxane block copolymers, polyethylene, polypropylene or other similar extrudable thermoplastic, polymeric materials, or composites thereof may be utilized in the present invention. Typically, a catheter may have a proximal end and a distal end, each of which is formed from a different material. It may, therefore, be two separate sheaths which are adhered together. The proximal end of the tubular sheath is typically made of a more flexible material than is the distal end. However, the entire sheath, both proximal and distal end, may be comprised of one material thereby forming a continuous sheath. Such materials are typically inherently non-lubricious.

The lumen of the outer sheath may comprise other tubular members which may serve to transport fluids, to protect guide wires or pull back wires, or the lumen may contain the guidewires or pull back wires themselves. Both during deployment of the medical device, and during retraction, it will be necessary to reduce the adhesion or friction which may be present between the materials. As discussed in U.S. Pat. No. 5,534,007 and incorporated herein by reference, the outer sheath may be a flexible tube which contains a pull wire lumen and a guide wire lumen. The outer sheath is comprised of high density polyethylene (HDPE) or Surlyn®. Optionally, the outer sheath may enclose an optional guide wire lumen which is made of a flexible, but incompressible construction, such as a polymer encapsulated braid or coil which may be comprised of stainless steel or nitinol encased in a polymer such as a polyimide, HDPE, teflon or polyurethane. The lubricious coating of the present invention may be coated on both the inner surface of the outer sheath to reduce adhesion and friction between the guide wire lumen and the inner surface of the outer sheath, and on the inner surface of the guide wire lumen to reduce friction between the inner surface of the guide wire lumen and the guide wire itself.

In another preferred embodiment of the present invention, a tubular member having an inner surface and an outer surface and comprised of a thermoplastic polymeric material slides over a metal wire. The inner surface of the tubular member is coated with the lubricious coating of the present invention to reduce the adhesion and friction between the polymeric material and the metal when the metal wire is moved through the polymeric tube. With the lubricious hydrophilic coating of the present invention, it is possible to achieve up to a 65%, preferably at least about 30% and more preferably at least about 50%, reduction in force for the wire movement friction.

A further benefit to utilizing the coating of the present invention is that the radius of the tubular members may be reduced, thereby reducing the profile of the catheter and improving the traceability.

The surface of the tubular member may be primed or pre-treated with the reactive compound having hydrophobic

and hydrophilic functionality thereon including those compounds having groups such as amine, amide, carboxyl, hydroxyl, and so forth. These groups are available on the surface for "binding" the water soluble lubricious coating in such a way that the coating will not wash away from the surface of the article. This reactive primer provides a uniform wettable surface which facilitates adherence of the lubricious coating along the elongated interior surface of the tube. The reactive compound may be silane or silicone oligomer which forms a crosslinked coating on the tubular surface upon application and drying. One method of treating priming or treating the inner surface of a tubular member involves a flush method whereby a solution of the lubricious coating is connected to a port of the tube via a syringe, and solution is thereby injected and passes through the entire tube. The silicone compound is dissolved in a solvent, preferably heptane or the like in a concentration of about 0.1% to about 10% of the crosslinkable compound, preferably from about 0.2% to about 5% concentration based on weight/volume. The excess solution trapped in the tubular member is removed through air pressure or nitrogen at 1-2 atmospheres. The crosslinking reaction is then carried out with heat at temperatures of about 30° C. to about 80° C., preferably from about 40° C. to about 65° C. and even more preferably at temperatures of about 45° C. to about 55° C.

The lubricious coating is prepared by making a solution of the water soluble lubricant in solvent at a concentration of about 1% to about 30% of the lubricant. Antioxidant may be added in an amount of about 0.01% to about 1.0% and preferably about 0.1% to about 0.5%. A preferable solvent is isopropanol. The lubricious coating may then be applied utilizing a flush method. A syringe may be connected to a port of the tubular member, the solution injected via a syringe or the like until approximately 3 ml/s passes through the tube. The lubricated tube is cleaned using air pressure or nitrogen at 1-2 atmospheres for at least 10 minutes, thereby removing excess solution.

Alternatively, the lubricious coating may be coextruded with the material from which the tubular member is being formed, such as polyethylene, Pebax®, polyester elastomer, and so forth, thereby forming a coating in this fashion. It is preferable that the lubricious coating be coextruded on the inside surface of the now dual layer tube.

In a preferred embodiment of the present invention, a hydrophobic ester is coextruded on the inside of the tubular member. The ester is subsequently hydrolyzed using an acid or base and heat, to form the hydrophilic lubricious coating on the inner surface of the tubular member.

EXAMPLES

Primer 1

A solution of crosslinkable silicone primer was prepared by dissolving 0.5 g of Silastic® MDX4 from Dow Corning Chemicals in Midland, Mich. in about 99.7 milliliters of heptane in a 100 ml column (concentration of 0.5% based on weight/volume). Silastic® MDX4 has a 50% concentration in a pseudocumene and isopropanol mixture as purchased. Heptane was purchased from Aldrich chemical in anhydrous form >99% purity with a water content of <0.005%. ps

Primer 2

A solution of crosslinkable silicone was prepared by dissolving about 0.2 g of MDX4 in heptane. The MDX4 was weighed in a 100 ml column with a cap and heptane is added to total 100 ml (about 0.2% concentration based on weight/volume).

In each example the inner surface of a catheter was treated with the MDX4 using a flush method. A 20 ml glass syringe

containing 10 ml of MDX4 solution was connected with the port of the catheter and 3 ml of solution is injected and passed through the whole catheter. The syringe was then moved to the other port. The treated catheter was then cleaned by air pressure or nitrogen at 1-2 atmospheres for in excess of 10 minutes to remove the excess solution trapped in the catheter. The cleaned catheter was then heated in an oven at 55° C. for at least 4 hours to carry out the crosslinking reaction.

Primer 3

A 3% weight/volume concentration of MDX4 to heptane was prepared as above.

Lubricious Coating 1

A solution of lubricant was prepared by dissolving 20 g of Pluronic® 31R1, polyoxypropylene-polyoxyethylene block copolymer from BASF and 0.02 g Vitamin E from Sigma in isopropanol (IPA) until a total of 100 ml is achieved resulting in a 20% weight/volume concentration. The IPA may be purchased from Aldrich Chemicals with >99% purity and a water content of <0.005%.

Lubricious Coating 2

A 10% solution of lubricant was prepared by dissolving 10 g of Pluronic® 31R1, 0.02 g Vitamin E in IPA until the total is 100 ml.

Lubricious Coating 3

A 20% solution of Cremophor® EL 35, ethoxylated castor oil, from BASF Corp. was prepared by dissolving 20 g of Cremophor® and 0.02 g Vitamin E in IPA until the total is 100 ml.

Lubricious Coating 4

A 20% solution of Cremophor® EL 35, ethoxylated castor oil, from BASF Corp. was prepared by dissolving 20 g of Cremophor® and 0.02 g Vitamin E in IPA until the total is 100 ml.

The inner surface of a catheter was lubricated using the flush method by connecting a 20 ml glass syringe containing about 10 ml lubricant solution to the port of the catheter, injecting the lubricant solution and passing it through the tip until 3 ml of solution was used. The catheter was then cleaned using air pressure or nitrogen gas at about 1-2 atmospheres for in excess of 10 minutes to remove any excess solution trapped in the catheter. The catheter is then heated to about 55° C. for about 1-2 hours and is conditioned over night at ambient temperature to ensure complete drying of the catheter.

Lubricious Coating 5

A 40% solution of Pluronic® 31R, polyoxypropylene-polyoxyethylene block copolymer from BASF, was prepared in isopropanol.

Example 1

A high density polyethylene balloon catheter with a lumen having an inner diameter of 0.0167" (0.0424 cm) was pretreated with Primer 1 followed with Lubricious Coating 3, above. Using a syringe, the lumen was then flushed with 3 mls of saline using a syringe. A stainless steel wire having an outer diameter of 0.0162" (0.0411 cm) was inserted and the wire movement force was measured using a computer controlled force test machine with a special fixture to model the tortuous shape of the coronary vessel. The wire was pulled at a rate of 8.25 mm/sec over a minimum of 300 mm. The test was done at ambient temperature. The force required to pull the wire through the catheter lumen was measured on the test specimen and on a control catheter which had no hydrophilic coating. The force required on the uncoated specimen was 250 g while that on the coated catheter was 85 g. A force reduction of 65% was noted.

FIG. 1 illustrates the force required for the uncoated control catheter and for Example 1.

Example 2

A high density polyethylene balloon catheter having a lumen with an inner diameter of 0.0169" (0.0429 cm) was pretreated with Primer 2 followed by Lubricious Coating 1. The same procedure utilizing the same size wire as in Example 1 was followed. The uncoated catheter had a wire movement force of 60 g while the coated catheter had a wire movement force of 30 g. A 50% force reduction was achieved.

FIG. 2 illustrates the force required for the uncoated control catheter and for Example 2.

Example 3

A polyethylene tube with a length of 75 mm, an inner diameter of 1.27 mm, an outer diameter of 1.31 mm and a wall thickness of 0.2 mm was first coated with Primer 3. The tube was dried in an oven at 55° C. for 2 hours. The tube was then coated a second time with Lubricious Coating 5 and dried in an oven at 55° C. for over 2 hours to ensure complete drying. A stainless steel rod having a length of 75 mm and a diameter of 1.27 mm was inserted into the coated polyethylene tube to a length of 25 mm.

A control sample was prepared by coating a polyethylene tube as described above with Primer 3 and followed by a 6% concentration of DC 360 silicone lubricant. A stainless steel rod was also inserted into this tube.

A pull test using an Instron Force Tested to measure the force, in grams, required to remove the stainless steel rod from the polyethylene tube was performed on both test specimens. The specimen with the DC 360 lubricant exhibited a pull force of 1.58 lbs (~720 g) while the specimen with Lubricious Coating 5 exhibited a lower pull force of 1.04 lb (~470 g), illustrating the superiority of the coating of the present invention.

What is claimed is:

1. A medical device comprising at least one tubular member having an inner surface and an outer surface wherein said inner surface of said tubular member is at least occasionally subjected to contact with at least one second surface, said tubular member comprising a hydrophilic coating disposed on said inner surface of said tubular member, wherein said hydrophilic coating is present to reduce the friction between the inner surface of said tubular member and said second surface caused by movement, and said inner surface of said tubular member is pretreated with a crosslinkable primer composition.

2. The medical device of claim 1 wherein said tubular member comprises a thermoplastic polymeric material.

3. The medical device of claim 1 wherein said tubular member comprises at least one material selected from the group consisting of homopolymers, copolymers and terpolymers of ethylene; homopolymers, copolymers and terpolymers of propylene; polyesters; polyamides; polyurethanes; vinylic copolymers; block copolymers; block copolymer ionomers; and mixtures thereof.

4. The medical device of claim 1 wherein said at least one second surface comprises at least one material selected from the group consisting of polymeric materials, metals and mixtures thereof.

5. The medical device of claim 1 wherein said hydrophilic coating comprises at least one material selected from the group consisting of polyalkylene glycols; alkoxy polyalkylene glycols; poly(saccharide); poly(vinylpyrrolidone); poly

(vinyl alcohol); poly(acrylic acid); poly(acrylamide); poly(maleic anhydride); copolymers thereof and mixtures thereof.

6. The medical device of claim 1 wherein said surface is pretreated with a crosslinkable surface modifying layer.

7. The medical device of claim 1 wherein said crosslinkable silicone is amino-functional polydimethylsiloxane.

8. The medical device of claim 1 wherein said crosslinkable primer composition is utilized at a concentration from about 0.1 to about 10%.

9. The medical device of claim 6 wherein said inner hydrophilic coating is formed by injecting a hydrophobic compound into said tubular member thereby forming a hydrophobic coating on said inner surface of said tubular member, and subsequently converting the surface of said hydrophobic coating to a hydrophilic coating.

10. The medical device of claim 9 wherein said hydrophobic compound is a polymer selected from the group consisting of poly(acrylates), poly(meth)acrylates, poly(vinyl esters), poly(maleate) esters, poly(fumarate) esters, polyamides, poly(acrylamides), copolymers and terpolymers thereof, and mixtures thereof.

11. The medical device of claim 9 wherein said hydrophobic polymer is converted to a carboxylic acid by hydrolysis.

12. The medical device of claim 1 wherein said hydrophilic lubricious coating further comprises Vitamin E.

13. The medical device of claim 1 coated by the process of:

a) pre-treating said inner surface of said tubular member with a crosslinkable primer composition; and

b) coating said inner surface of said pre-treated tubular member with a water soluble lubricious coating.

14. The medical device of claim 13 wherein said pre-treating (a), and said coating (b) are accomplished by means of a flushing method.

15. The medical device of claim 1 wherein said tubular member comprises a polymeric tube and said at least one second surface is a metallic wire.

16. The medical device of claim 15 wherein the friction is reduced between said inner surface of said tubular member and said at least one second surface by at least about 30%.

17. The medical device of claim 1 wherein said medical device is a catheter assembly.

18. The catheter assembly of claim 17 wherein said catheter is selected from the group consisting of fixed wire catheters, over the wire catheters and rapid exchange catheters.

19. The catheter assembly of claim 17 wherein said catheter is a stent deployment catheter.

20. The catheter assembly of claim 17 wherein said inner surface is a polymeric material and said at least one second surface is a metal wire.

21. The catheter assembly of claim 17 wherein said catheter is utilized to deploy a medical device selected from the group consisting of a stent, a stent-graft, a graft and a vena cava filter.

22. The catheter assembly of claim 17 wherein wire movement friction is reduced by greater than about 30%.

23. A stent deployment catheter assembly comprising:

a. at least one tubular member for retention and release of a stent selected from the group consisting of a retractable sheath and at least one stent retaining sleeve wherein said tubular member has an inner surface and an outer surface wherein said inner surface comprises a hydrophilic, lubricious, coating; and

b. a stent;

wherein said inner surface of said tubular member is at least occasionally subjected to contact with said stent and said hydrophilic coating reduces friction between said inner surface of said tubular member and said stent.

24. The catheter assembly of claim 23 wherein said hydrophilic coating comprises at least one compound selected from the group consisting of polyalkylene glycol; alkoxy polyalkylene glycol; poly(saccharide); poly(vinylpyrrolidone); poly(vinyl alcohol); poly(acrylic acid); poly(acrylamide); poly(maleic anhydride); copolymers and mixtures thereof.

25. The catheter assembly of claim 23 wherein said inner surface of said tubular member is pretreated with a reactive primer composition.

26. The catheter assembly of claim 25 wherein said reactive primer composition comprises at least one crosslinkable silicone.

27. The catheter assembly of claim 26 wherein said silicone comprises amino groups.

28. The catheter assembly of claim 25 wherein said primer composition comprises at least one hydrophobic compound which is capable of undergoing a chemical reaction whereby said hydrophobic surface of said inner surface of said tubular member is converted to a hydrophilic lubricious coating.

29. The catheter assembly of claim 28 wherein said hydrophobic compound is a polymer selected from the group consisting of poly(acrylates), poly(meth)acrylates, poly(vinyl esters), poly(maleate) esters, poly(fumarate) esters, polyamides, poly(acrylamides), copolymers and terpolymers thereof, and mixtures thereof.

30. The catheter assembly of claim 28 wherein said primer composition comprises at least one hydrophobic polymer which is capable of forming a carboxylic acid through hydrolysis.

31. The catheter assembly of claim 23 wherein said stent is a tubular, flexible, expandable stent.

32. A medical device for insertion into the body, comprising a first surface which is at least periodically subjected to contact with a second surface; said first surface, comprising:

a) a crosslinkable silicone primer having substituents capable of forming hydrogen bonds; and

b) a lubricious, biocompatible hydrophilic polymer; wherein said crosslinkable silicone primer improves retention of said hydrophilic polymer to said polymeric surface, and said hydrophilic polymer reduces friction between said first polymeric surface and said second surface.

33. A method of forming a lubricious hydrophilic coating on the inner surface of a tubular member comprising the steps of:

a) coextruding a first hydrophobic polymer simultaneously with a second hydrophobic polymer wherein said first and second polymers form a tubular member having a first inner hydrophobic surface formed from said first hydrophobic polymer and a second outer hydrophobic surface formed from said second polymer; and

b) converting said first inner hydrophobic surface to a lubricious hydrophilic surface.

34. A method of forming a lubricious hydrophilic coating on the inner surface of a tubular member comprising the steps of:

a) coextruding a first hydrophobic polymer simultaneously with a second hydrophobic polymer wherein

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said first and second polymers form a tubular member having a first inner hydrophobic surface formed from said first hydrophobic polymer and a second outer hydrophobic surface formed from said second polymer; and

- b) converting said first inner hydrophobic surface to a lubricious hydrophilic surface.

35. The catheter assembly of claim 1 wherein said primer composition includes a titanate, a zirconate, or a mixture thereof.

36. A medical device comprising at least one tubular member having an inner surface and an outer surface wherein said inner surface of said tubular member is at least occasionally subjected to contact with at least one second surface, said tubular member comprising a hydrophilic coat-

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ing disposed on said inner surface of said tubular member, wherein said hydrophilic coating is present to reduce the friction between the inner surface of said tubular member and said second surface caused by movement, and said inner surface of said tubular member is pretreated with a primer compound comprising substituents that improve the retention of said hydrophilic coating by hydrogen bonding.

37. The medical device of claim 36 wherein said substituents are selected from the group consisting of amine, amide, carboxyl, hydroxyl, thiol, phosphorous, and mixtures thereof.

38. The method of claim 33 wherein said converting step is accomplished through a chemical reaction.

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(12) **United States Patent**
Lee(10) **Patent No.:** **US 6,817,414 B2**
(45) **Date of Patent:** **Nov. 16, 2004**(54) **ACID COATED SAND FOR GRAVEL PACK
AND FILTER CAKE CLEAN-UP**(75) **Inventor:** Li-Jien Lee, Sugar Land, TX (US)(73) **Assignee:** M-I LLC, Houston, TX (US)(*) **Notice:** Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 0 days.(21) **Appl. No.:** 10/065,141(22) **Filed:** Sep. 20, 2002(65) **Prior Publication Data**

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166/311; 166/376(58) **Field of Search:** 166/278, 279,
166/311, 312, 376; 428/403-407; 507/901(56) **References Cited****U.S. PATENT DOCUMENTS**3,026,938 A * 3/1962 Huitt et al. 166/280.1
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Primary Examiner—John Kreck(74) **Attorney, Agent, or Firm**—Howrey Simon Arnold &
White LLP(57) **ABSTRACT**

A method of the preparation and utilization of polymerized alpha-hydroxycarboxylic-acid-coated proppants for gravel pack and removal of filter cake that was deposited by reservoir drilling fluid. In a preferred example, polyglycolic-acid-coated sand is used to replace conventional gravel pack sand typically used for gravel packing. Under downhole conditions, the acidic by-product generated from the hydration of polyglycolic-acid-coated sand can break down acid-soluble and/or acid-breakable components embedded in the filter cake. This reaction enhances the filter cake removal and the flow of hydrocarbon from the producing formation. The polyglycolic-acid-coated sand may be produced by polymerizing a glycolic acid with a natural or synthetic proppant like 20-40 mesh commercial sand, at temperatures of about 210° F. or higher.

9 Claims, No Drawings

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ACID COATED SAND FOR GRAVEL PACK AND FILTER CAKE CLEAN-UP

BACKGROUND OF INVENTION

To produce oil and gas from hydrocarbon reservoir, a borehole of tapered and often times deviated geometry is first drilled through geological formations. The hydrocarbon-bearing formation then is drilled with a specially designed reservoir drilling fluid, which may comprise various additives, such as starches and calcium carbonate, that are soluble or breakable by acid, oxidizers, or enzymes, or a combination of these chemicals.

Once the desired borehole in the hydrocarbon reservoir is drilled, production tubes and/or screens are run to the bottom of the borehole and placed against the desired formations for hydrocarbon production. Often times, especially when the hydrocarbon-bearing formations consist of poorly cemented sands, some kind of sand control methods or devices are used to prevent sand particles from the formation from entering and plugging up the production screens and tubes in order extend the life of the well.

One of the typical sand control methods is to fill the annular space between the wellbore and the production screens with specially sized sand, which is usually larger than the formation sand and commonly known as gravel pack sand. The process to place the sized sand behind the production screen is known as a gravel pack operation.

In order to be able to fill the annular space with sand completely and successfully, the hydrocarbon-bearing formation should have been previously covered with a thin layer of firm and impermeable filter cake formed by the reservoir drilling fluid. This thin and impermeable filter cake may prevent the gravel pack fluid from entering the formation, which when occurring at an uncontrollable rate, would result in gravel pack failure.

After the gravel pack sand has been successfully placed, the filter cake existing between the gravel pack sand and the formation needs to be removed before the flow of hydrocarbon is initiated. Without the removal of the filter cake, plugging of the production screen by the filter cake could occur and would result in a production impairment.

To destroy the filter cake that is now behind the gravel pack sand, various chemicals, breakers and mechanical devices have been developed and used. For example, hydrochloric acid is often delivered by a separate operation to soak the gravel pack sand and filter cake with the aid of wash cups. The mechanical wash cups attached to the end of a work string must be picked up at the surface and lowered to the bottom through the inside of the screen. The hydrochloric acid is then pumped through the gravel pack sand repeatedly. The goal of this exercise is to destroy a large amount of the acid-soluble and acid-breakable components in the filter cake.

Other breakers, such as oxidizers and enzymes, may also be delivered to destroy oxidizer- and enzyme-breakable organic components, such as starch polymers. However, these breakers are considered less efficient in several ways. First, they are not effective in destroying acid-soluble and acid-breakable inorganic components in the filter cake, such as calcium carbonate. As a result, acid-soluble and breakable components will remain behind the gravel pack sand and may subsequently cause impairment during the production of the well. Second, many oxidizing breakers have compatibility issues with certain brines. They may react with the brine and create undesirable by-products, such as Cl_2 and

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Br_2 gases. This reaction will occur even before the breakers were pumped down to attack the filter cake. Third, in addition to brine compatibility issues, enzyme breakers also have a temperature issue. Most enzyme breakers will lose reactivity in highly concentrated divalent brines, and at temperatures above 200° F.

The above breakers are normally pumped on a separate trip after the gravel pack sand has been set. They are not pumped during the gravel pack operation because they can create precarious conditions for the operation. For instance, the acid-based breakers can destroy the filter cake during gravel pack operation, and consequently result in high fluid loss and premature failure in the gravel pack operation.

Pumping oxidizers and enzyme breakers with gravel pack sand may cause inconsistent application of oxidizers and enzyme breakers to the filter cakes. Since most of the solid oxidizers and enzyme breakers are organic materials with relatively low specific gravity and small particle size, they tend to be pushed toward the screen rather than toward the filter cake where the reaction needs to take place. As a result, the concentration and distribution of these breakers in the gravel pack sand is likely to be erratic, making the filter cake removal less effective.

Microencapsulation is one technique used to deliver well-bore chemicals downhole. The microencapsulation process and application of microencapsulated oil field chemicals, such as scale inhibitors, corrosion inhibitors, surfactants, bactericides, paraffin dispersants, pourpoint modifiers, cement additives, fracture fluid cross linkers, emulsion breaking chemicals, chemical tracers, radioactive tracers, and asphaltene treatment chemicals, using condensation product of hydroxyacetic were disclosed in U.S. Pat. No. 4,986,354. The encapsulated special chemicals are injected along with water into oil wells. Disintegration of the encapsulating polyglycolic polymer in the presence of water allows the encapsulated chemicals to be released to achieve desired reactions.

Microencapsulation of pesticides, insect growth regulators, and other organic compounds in biodegradable polymers from the group consisting of polylactic acid and copolymers of lactic and glycolic acids was disclosed in U.S. Pat. No. 4,272,398.

None of the methods above efficiently deliver the necessary breakers to a filter cake. Thus, there exists an on-going need and desire for breakers which provide a slow release mechanism to initiate the disintegration of filter cakes so that gravel pack operations can be continued.

SUMMARY OF INVENTION

The invention is related to the preparation and utilization of polymerized alpha-hydroxycarboxylic acid coated propants for gravel pack, and the removal of a filter cake that was deposited by reservoir drilling fluid. A preferred example is polyglycolic-acid-coated sand, which is used to directly replace conventional gravel pack sand typically used for gravel packing. Under downhole conditions, the acidic by-product generated from the hydration of polyglycolic-acid-coated sand can break down acid-soluble and/or acid-breakable components embedded in the filter cake. This reaction enhances the filter cake removal and the flow of hydrocarbon from the producing formation.

DETAILED DESCRIPTION

The present invention develops a relatively dense breaker that can be used as gravel pack sand and placed evenly

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across an impermeable filter cake deposited by a reservoir drilling fluid using a conventional gravel pack operation. Under downhole conditions, the breaker product will slowly release an acidic by-product to dissolve or break-down acid-soluble and acid-breakable components in the filter cake. The invention involves the coating of a proppant, such as sized, industrial grade gravel pack sand, with a polymerized alpha-hydroxycarboxylic acid. A preferred polymer is polyglycolic acid which is formed in-situ from monomeric glycolic acid. It should be noted that the polymerized alpha-hydroxycarboxylic-acid-coated proppant may be mixed with a quantity of un-coated proppant, such as conventional gravel pack sand and polyglycolic-acid-coated sand. The breaker-coated sand can be used as gravel pack sand and can be evenly distributed over the filter cake.

Glycolic acid is a member of the alpha-hydroxy acids. The monomers can be polymerized into polymeric forms by condensation polymerization. Self-polymerization can be initiated by heating the monomer to a temperature above the melting point of the polymeric form. The polymeric form of alpha-hydroxy acids, once formed and re-dispersed in water, can slowly hydrolyze and release an acidic by-product. The rate of hydrolysis is affected by temperature. Other alpha-hydroxy acids useful in the invention are malic, lactic, gluconic, citric, mandelic, saccharic, mucic, tartaric and mixtures thereof. Any of the acids above may be mixed with glycolic acid.

Polyglycolic acid polymers are known in the art and described in U.S. Pat. Nos. 3,468,853 and 3,875,937 incorporated herein by reference. The polymeric form of alpha-hydroxy acids made from a condensation process has been used in the medical industries for manufacturing of biodegradable medical articles such as sutures, capsules, etc. A method for production of polyglycolic acid to make medical articles is disclosed in U.S. Pat. No. 6,150,497.

Proppants useful in the invention are any particulate substrate useful for gravel packing. Examples of suitable substrates are natural and synthetic silica sand, glass beads, quartz, ceramics, thermoplastic resin, sintered bauxite, and metal oxides and mixtures thereof.

When a completed well is ready for gravel pack operation, the polyglycolic-acid-coated proppant is added to the gravel pack fluid and pumped downhole to fill the annular space between the production screen and formation in place of the typical gravel pack sand. The gravel pack fluid may consist of water and brines containing various electrolytes and their blends, such as but not limited to NaCl, KCl, CaCl₂, CaBr₂, ZnBr₂, etc.

Under downhole conditions, the polyglycolic acid coating will generate acidic by-products that can react with the acid-soluble and acid-breakable components in the filter cake. Because of the slow release rate of the acidic by-product, it is preferred that the well be shut-in for a given period of time to complete the dissolution and break-down reaction.

The polyglycolic-acid-coated sand can be produced by heating a glycolic acid monomer, such as a 70% technical grade glycolic acid solution, with a natural or synthetic proppant, such as 20-40 mesh commercial sand, at temperatures of about 210° F. or higher until the sand-glycolic acid mixture turns lightly brown, or when the moisture content of the mixture is reduced to less than 5% by weight of dry sand.

Alternatively, the glycolic acid monomer can be pre-heated at a temperature of at least 210° F. until polymerization has started. While maintaining the polyglycolic acid in a liquid form at the above temperature, the proppant can be

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slowly added and constantly stirred until the ratio of the polyglycolic acid to the proppant is in the range of about 5 to about 20% per dry weight of the proppant, preferably about 8% to about 10%. Employment of other methods of coating the proppant with the polyglycolic acid, such as spray drying, also may be used.

Once the polymerization reaction is completed, the final product is allowed to cool down to room temperature. The product may be lightly ground, using a mortar and pestle or other grinding device, and sieved through a screen, such as a 60-mesh screen, to remove fine particles.

Examples are given below to illustrate the procedures that can be used to prepare polyglycolic-acid-coated sand. However, it should be noted that the production of the polyglycolic-acid-coated sand is not limited to the procedures used by the examples.

The following examples are included to demonstrate preferred embodiments of the invention. It should be appreciated by those of skill in the art that the techniques and compositions disclosed in the examples which follow represent techniques discovered to function well in the practice of the invention, and thus can be considered to constitute preferred modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the spirit and scope of the invention.

General Information Relevant to the Examples: To evaluate the effects of the polyglycolic-acid-coated sand on filter cake clean up, the test procedure below was used. The test equipment and materials used are considered typical for those who are skilled in the art.

1. A reservoir drilling fluid was first prepared using a given fluid formulation that had been previously selected for a possible field well drilling application.
2. A filter cake was built on a water-saturated ceramic disk having an average 5-micron pore opening size in a double-ended high temperature high pressure fluid loss cell by pressing the reservoir drilling fluid against the ceramic disk with about 300 psi nitrogen differential pressure at about 140° F.-180° F. for approximately 16 hours.
3. After the filter cake had been built, the reservoir drilling fluid inside the cell was decanted and the inside of the cell was rinsed with water to remove the remaining fluid residues.
4. The cell was filled with about 70 mls of a brine to be used for gravel packing. The testing breaker, e.g., the polyglycolic-acid-coated sand or a blend of uncoated gravel pack sand with a chemical breaker, was slowly poured into the brine. No stirring or mixing was performed when adding the breaker.
5. The cell was reassembled, pressurized, and heated to desired temperature to soak the filter cake along with the breaker and gravel pack sand. The drainage valve at the bottom of the cell could be either closed or open depending on the purpose of testing.
6. With the bottom drainage valve open, the soaking brine could flow through the disk as soon as the breaker had reacted with the filter cake and created a communication channel through the filter cake. The time required for this to happen was monitored and measured.
7. With the bottom drainage valve closed, the cell was said to be in a shut-in condition and the soaking brine was not allowed to flow out until a pre-determined soaking

time has been reached. The rate at which the brine was drained was monitored to evaluate the efficiency of filter cake clean up.

After the soaking test, the condition of the filter cake inside the cell, such as the amount of residue left on the disk, was visually examined. Permeability of the ceramic disk before or after the soaking also could be measured to evaluate the effectiveness of the removal of filter cake.

EXAMPLE 1

A batch of polyglycolic acid coated sand was prepared using the following ingredients and procedures:

1. A mixture consisting of 380 grams of 20-40 mesh industrial quartz sand from Unimin Corporation and 190 grams of technical grade, 65-70 weight % glycolic acid solution from J. T. Baker was mixed together in a 2-liter crystallizing dish.
2. The dish was placed on a hot plate and heated under a ventilated hood. A temperature of at least 210-220° F. was obtained and maintained for about 8-10 hours.
3. The mixture was stirred frequently until the mixture turned into a light-brown colored, somewhat viscous and sticky mixture.
4. When the color of the final mixture changed to light-brown, the heating was terminated.
5. The mixture was cooled to room temperature while stirring. Large aggregates formed during cooling were broken up into individual grains using mortar and pestle.
6. The loose polyglycolic acid-coated sand grains were sieved through a 60-mesh screen to remove fine-grained, uncoated polyglycolic acid. The sieved polyglycolic acid-coated sand was used for the filter cake clean up test.

Based on mass balance, the sieved polyglycolic acid-coated sand contains approximately 13% by weight of polyglycolic acid per dry weight of sand. Although the industrial sand used has a 20-40 mesh size, other sizes of industrial sand can also be used to prepare the polyglycolic acid-coated sand.

EXAMPLE 2

Using the polyglycolic acid-coated sand that was previously prepared with the method described in Example 1, and the test procedures described above, the filter cake removal efficiency of the polyglycolic acid-coated sand was evaluated.

completely destroyed at the end of the soaking with the polyglycolic acid-coated sand. Return permeability evaluation indicated that the ceramic disk was not severely damaged in terms of fluid conductivity. The test results are given in the following table (Table 1).

TABLE 1

Results of evaluation of polyglycolic acid-coated sand as a breaker to remove filter cake deposited from a 13.0 ppg CaBr ₂ based reservoir drilling fluid. The polyglycolic acid content was about 21%.				
Type of Mud to build cake	Breaker	Soaking Time & Temperature	Filter Cake after Soaking	Return Permeability
13 ppg CaBr ₂ based	approx. 22 g PGA coated	4.5 hrs at 180 F. w/Valve	Mostly intact with	n/a

TABLE 1-continued

Results of evaluation of polyglycolic acid-coated sand as a breaker to remove filter cake deposited from a 13.0 ppg CaBr ₂ based reservoir drilling fluid. The polyglycolic acid content was about 21%.				
Type of Mud to build cake	Breaker	Soaking Time & Temperature	Filter Cake after Soaking	Return Permeability
10 Reservoir drilling fluid	sand in 13 ppg CaBr ₂ brine	Open	a few pin holes	
13 ppg CaBr ₂ based	approx. 22 g PGA coated	31.5 hrs at 180 F. w/Valve	>90% destroyed	770 md (3-μ disk)
15 Reservoir drilling fluid	sand in 13 ppg CaBr ₂ brine	Closed		

Return Permeability is the average initial permeability of 5-micron disk is about 800 md.

EXAMPLE 3

A series of tests were conducted to illustrate the effects of temperature on the filter cake clean up capability of the polyglycolic acid-coated sand. Filter cakes were built at specific temperatures and then soaked with the polyglycolic acid-coated sand at the same specific temperatures. The valves were closed during the soaking except at 48 and 72 hours of testing when the valves were opened to drain the soaking brine.

After 48 hours of soaking, none of the cells was able to drain the soaking brine, indicating no effective communication was established through the filter cake. After 72 hours of soaking, the soaking brine was effectively drained; however, there was a difference in the draining rate. Examination of the ceramic disks recovered after the test showed varying amounts of filter cake residues left on the disks, which seems to indicate that the effectiveness of the clean up by polyglycolic acid-coated sand was temperature dependent. Thus, shut in time required for complete filter cake removal should be adjusted depending on the temperature. Test results are disclosed in Table 2 below.

TABLE 2

Results of evaluation of polyglycolic acid-coated sand as a breaker to remove filter cake deposited from a 12.5 ppg CaBr ₂ based reservoir drilling fluid. The polyglycolic acid content was about 13%.				
Type of Mud to build cake	Breaker	Soaking Time & Temperature	Filter Cake after Soaking	
12.5 ppg CaBr ₂ based Reservoir drilling fluid	20 grams PGA coated sand in 12.5 ppg CaBr ₂ brine	72 hrs at 140 F. with Valve Closed	approx. 50% destroyed	
12.5 ppg CaBr ₂ based Reservoir drilling fluid	20 grams PGA coated sand in 12.5 ppg CaBr ₂ brine	72 hrs at 160 F. with Valve Closed	approx. 90% destroyed	
12.5 ppg CaBr ₂ based Reservoir drilling fluid	20 grams PGA coated sand in 12.5 ppg CaBr ₂ brine	72 hrs at 180 F. with Valve Closed	greater than 90% destroyed	

EXAMPLE 4

The following table (Table 3) illustrates the generation of acidic components from polyglycolic acid-coated sand in various fluids as compared with un-coated sand placed in

similar fluids, as indicated by pH measurement after each fluid was exposed to 140° F. for 4 days. The concentration of uncoated sand and polyglycolic-acid-coated sand was 10% by weight per volume of the fluid. The use of polyglycolic-acid-coated sand with divalent brines is more beneficial than with freshwater.

TABLE 3

Results of the generation of acidic components of
polyglycolic-acid-coated sand in various fluids

	Uncoated Sand (pH)	PGA - Coated Sand (pH)
Freshwater	9.1	2.9
10 ppg NaCl Brine	8.1	1.6
12.5 ppg NaCl Brine	8.3	1.6
11.6 ppg CaBr ₂ Brine	6.1	less than 0.1
14.2 ppg CaBr ₂ Brine	4.8	less than 0.1

While the compositions and methods of this invention have been described in terms of preferred embodiments, it will be apparent to those of skill in the art that variations may be applied to the process described herein without departing from the concept, spirit and scope of the invention. All such similar substitutes and modifications apparent to those skilled in the art are deemed to be within the spirit, scope and concept of the invention as it is set out in the following claims.

What is claimed is:

1. The process of using proppants coated with polymerized alpha-hydroxycarboxylic acid for a gravel pack operation to fill the annular space between the formation and production screen and filter cake removal comprising: combining said proppants with a gravel pack fluid to create a mixture;

pumping said mixture downhole into the annular space between the formation and production screen; and,

letting said proppants contact the filter cake until the acid-soluble and acid-breakable components in the filter cake are broken down.

2. The process of claim 1 wherein the proppants are polyglycolic-acid coated sand.

3. The process of claim 1 wherein the gravel pack fluid comprises water, brines, and electrolytes.

4. The process of claim 1 wherein the gravel pack fluid comprises NaCl, KCl, Ca Cl₂, CaBr₂ and mixtures thereof.

5. The process of claim 1, wherein the mixture is left in the well for at least 24 hours.

6. The process of claim 1 wherein the proppants coated with polymerized alpha-hydroxycarboxylic acid are mixed with un-coated proppants.

7. The process of claim 6 wherein the proppants are polyglycolic-acid coated sands, and the un-coated proppants are conventional gravel pack sand.

8. The process of using proppants coated with polymerized alpha-hydroxycarboxylic acid for a gravel pack operation to fill the annular space between the formation and production screen comprising:

combining said proppants with a gravel pack fluid to create a mixture, and pumping said mixture downhole into the annular space between the formation and production screen.

9. The process of claim 8 wherein the proppants are coated with polyglycolic acid.

* * * * *



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McDougall et al.

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[54] COMPOSITION COMPRISING
ENCAPSULATED SUBSTRATE AND
THERMOPLASTIC POLYMER
OVERCOATING

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5,102,558, which is a continuation-in-part of Ser. No.
446,572, Dec. 4, 1989, abandoned, which is a continuation-
in-part of Ser. No. 446,831, Dec. 6, 1989, abandoned,
which is a continuation-in-part of Ser. No.
446,958, Dec. 6, 1989, abandoned.

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428/402.24, 403, 407, 500, 517, 334; 427/212,
214; 71/6, 28, 119, 64.02; 524/547, 364;
525/344

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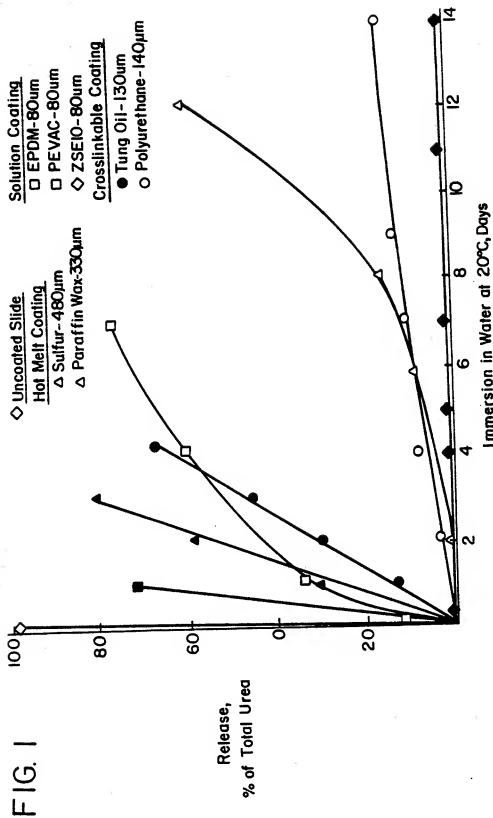
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[57]

ABSTRACT

An encapsulated breaker chemical composition used in a fracturing process in the protection of an oil or gas stimulation operation which comprises: a breaker chemical; and a pinhole free coating of a neutralized sulfonated elastomeric polymer of about 2 to about 80 microns thick deposited onto the surface of the breaker chemical, wherein said neutralized sulfonated polymer encapsulates the breaker chemical, wherein the neutralized sulfonated polymer is permeable to the breaker chemical and the neutralized sulfonated polymer is non-reactive to the breaker chemical.

6 Claims, 1 Drawing Sheet



COMPOSITION COMPRISING ENCAPSULATED SUBSTRATE AND THERMOPLASTIC POLYMER OVERCOATING

This is a division of application Ser. No. 637,401, filed Jan. 4, 1991, now U.S. Pat. No. 5,102,558, which application is a continuation-in-part of copending application Ser. No. 07/446,572, filed on Dec. 4, 1989 and Ser. Nos. 07/446,831, and 07/446,958, each filed on Dec. 6, 1989, all now abandoned.

FIELD OF THE INVENTION

The present invention relates to encapsulated breaker chemicals which are used in fracturing fluid systems. The encapsulated breaker chemical comprises a breaker chemical which is encapsulated within an elastomeric polymeric coating which is suitably permeable to permit the breaker chemical to be released through the polymeric coating into the fracturing fluid. The polymeric coating of the instant invention comprises a neutralized sulfonated elastomeric polymer.

DESCRIPTION OF PRIOR ART

Solids (e.g., substrates, pipes, slabs, sheets, etc.) can be protected from the external environment with the use of barrier or protective coating materials. For protection from water or moisture, polymer or organic materials are widely used. For coat effectiveness, however, these materials are generally applied as thin films. The thickness of the film depends upon the desired degree of water protection. The thicker the film the more likely that water penetration would be slowed down. In practice, applying an effective thin coating is difficult because of the various stresses tending to make the film discontinuous (e.g., film-rupture, pin holes). Films will rupture when a threshold stress is exceeded. The lateral stress tending to rupture a film is inversely proportional to an exponential power of the film thickness. The thinner the film, the more easily it will rupture.

There are many applications for thickened or gelled solutions of polymers in aqueous or organic liquids which are quite diverse. There are also a number of physical and chemical techniques for preparing such systems. Such systems are used for viscosity control, solids carrying and fluid loss control in fracturing fluids or to place sand or gravel packs downhole in oil or gas wells.

Many types of fluids are available for use in wellbore fracturing procedures. Chief properties required by the fracturing fluids are low leak off rate, the ability to carry a propping agent and low pumping friction loss. The fluid should also be easy to remove from the formation; it should be compatible with natural formation fluids; and it should cause a minimum of damage to the formation permeability. These properties can be achieved with oil based fluids, water based fluids, emulsions, foam, and other multi-phase suspensions.

A fracturing process used in a well treating operation involves the introduction into the well of a fluid under sufficient hydraulic pressure to produce or enlarge fractures in the subterranean formation. The fracturing fluid usually contains a propping agent such as sand, sintered alumina, glass beads, aluminum spacers, urea prills or nutshells, wherein the propping agent is deposited within the fracture in order to maintain the fracture in an open mode or alternatively, an acid is contained

within the fracturing fluid wherein the acid reacts with acid reactable components of the subterranean formation thereby creating and enlarging the fracture so that one obtains increased flow of fluids from the subterranean formation. The propping agent is suspended within a polymeric gel or a highly viscous polymeric solution. After the highly viscous fluid has been pumped into the fracture and the fracture is formed or enlarged, it is desirable that the highly viscous fluid be converted into a low viscosity fluid so that the fluid can be removed from the fracture thereby leaving the propping agent within the fracture. The removal of the fluid is necessary so that the oil or gas can flow back through the fracture into the well bore. The conversion of the highly viscous solution into the lower viscosity fluid is called breaking the gel. The breaking of the gel is accomplished by adding a breaker chemical to the gel at the appropriate time. It is critical that the breaking process does not prematurely occur prior to the completion of the fracturing process. The usual method of addition of the breaker chemical is to pump it through the well bore into the fracture upon completion of the fracturing process, but this presents the problem of having the breaker chemical completely mix with the viscous fluid within the fracture to maximize breaking of the gel.

The use of breaker systems to break viscous water gels and fluids is not of itself new. Systems describing these chemicals are found, for example, in U.S. Pat. Nos. 3,167,510; 3,816,151; 3,960,736; 4,250,044 and 4,506,734. But most of these breakers are applied after introduction of the fracturing fluid into the wellbore because these breakers immediately start to degrade the viscosity enhancer in the fracturing fluid upon contact thereby lowering the efficiency of the fracturing process. In such cases, additional time and labor are needed to effect the reduction of the viscosity of fracturing fluids introduced into the subterranean formation. The use of organic breakers such as alkyl formate may alleviate this problem, since they can be applied along with the fracturing fluid. But these types of breakers rely on certain subterranean conditions, such as elevated temperature and time, to effect a viscosity reduction of the fracturing fluid. Since these organic breaker chemicals work on chemical change, such as hydrolysis, they are slow in effecting viscosity reduction. Furthermore, their performance can be unpredictable.

Accordingly, the incorporation of a breaker chemical into the fracturing fluid prior to the pumping of the fracturing fluid into the well bore and well fractures is desirable. The breaker chemical must be in a passive, non-reactive state such that it cannot react with the viscous fluid of the fracturing well prior to the injection of the fracturing fluid into the fractures, but the breaker chemical must be capable of reacting with the viscous fluid of the fracturing fluid within the fracture upon the completion of the fracturing process. The present invention teaches a method of accomplishing this objective.

SUMMARY OF THE INVENTION

The present invention relates to encapsulated breaker chemicals which are used in a process for forming and enlarging fractures in a subterranean formation in oil well stimulation operations. The encapsulated breaker chemical is added above ground to the fracturing fluid which comprises a viscous or gelled polymeric solution, a propping agent, the encapsulated breaker chemical

and other additives commonly used in fracturing fluids. The encapsulated breaker chemical comprises a breaker chemical having an elastomeric coating deposited on the surface of the breaker chemical, wherein the elastomeric coating, having a thickness of at least about 1 micron, preferably from about 1 to about 100 microns, more preferably from about 2 to about 80 microns, and most preferably from about 5 to about 70 microns, encapsulates the breaker chemical. The coating must be of a composition which is not degraded by the breaker chemical and will be permeable to the breaker chemical at conditions of use. The coating of the instant invention comprises a neutralized and ionically cross linked sulfonated elastomeric polymer, preferably a neutralized sulfonated terpolymer of ethylene, propylene and non-conjugated diene (EPDM terpolymer).

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 illustrates a plot of release versus immersion time in water for the coatings of the instant invention and control samples.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to an encapsulated breaker chemical composition used in a fracturing process in the production of oil or gas which comprises: (a) a breaker chemical; and (b) a pinhole free coating of a neutralized sulfonated elastomeric polymer having a preferred thickness of about 2 to about 80 microns deposited onto the surface of the breaker chemical, wherein said neutralized sulfonated polymer encapsulates said breaker chemical, wherein said neutralized sulfonated polymer will be permeable to said breaker chemical under conditions of use and said neutralized sulfonated polymer is non-reactive to said breaker chemical.

The sulfonated (sulfo) elastomeric polymers which are preferred for the purposes of this invention are water insoluble and include sulfonated copolymers of ethylene and propylene, sulfonated terpolymers of ethylene, propylene and a diene, preferably a non-conjugated diene (EPDM), sulfo Butyl rubber, sulfo isoprene/styrene rubber, sulfo isoprene/butadiene rubber, sulfo isoprene/butadiene/styrene copolymers, sulfo isobutylene/styrene copolymers, sulfo isobutylene/para methyl styrene copolymers, and complexes of the aforementioned polymers with a nitrogen containing polymer such as vinyl pyridine copolymer.

The more preferred neutralized sulfonated elastomers of the instant invention are selected from the group consisting of sulfonated Butyl rubber, sulfonated EPDM terpolymer and a complex of sulfonated EPDM terpolymer with a vinylpyridine copolymer.

The water insoluble sulfonated polymers of the instant invention will comprise from about 4 to about 200 milliequivalents of pendant sulfonate groups per 100 grams of polymer, more preferably from 10 to 100 meq. pendant sulfonate groups. The sulfonated elastomers utilized in the instant invention are neutralized with transition elements selected from Groups IVA, VA, VIA, VIIA, VIIIA, IB, and IIB of the Periodic Table of Elements and lead, tin, and antimony, as well as ammonium and amine counterions. Zinc and sodium neutralizing ions (as ionic salts, e.g., acetate or hydroxide) are preferred.

Neutralization of the cited polymers with appropriate metal hydroxides, metal acetates, metal oxides or am-

monium hydroxide, etc. can be conducted by means well known in the art. For example, the sulfonation process as with Butyl rubber, containing a small 0.3 to 1.0 mole percent unsaturation, can be conducted in a suitable solvent, such as toluene, with acetyl sulfate as the sulfonating agent such as described in U.S. Pat. No. 3,836,511, incorporated herein by reference. The resulting sulfonic acid derivative can then be neutralized with a number of different neutralization agents such as sodium phenolate and similar metal salts. The amounts of such neutralization agents employed will normally be stoichiometrically related to the amount of free acid in the polymer. It is preferred that the amount of neutralizing agent employed is in an excess percent to ensure full neutralization. The use of an excess of such neutralization agent is necessary to effect at least 50 percent neutralization of the sulfonic acid groups present in the polymer, preferably at least 90 percent, and most preferably essentially complete neutralization of such acid groups should be effected.

Thus, the degree of neutralization of said sulfonate groups may vary from 50 to 100 mole percent. With the utilization of neutralized sulfonates in the instant invention, it is preferred that the degree of neutralization be substantially complete, that is, with no substantial free acid present and without substantial excess of the base, other than that needed to ensure neutralization. The neutralized sulfonates possess greater thermal stability compared to their acid form and are ionically cross-linked. Thus it is clear that the polymers which are normally utilized in the instant invention comprise substantially neutralized pendant groups and, in fact, an excess of the neutralizing material may be utilized without defeating the objects of the instant invention.

The sulfonated elastomer polymers of the instant invention may vary in number average molecular weight from 1,000 to 10,000,000 preferably 5,000 to 1,000,000 most preferably from 10,000 to 600,000. These polymers may be prepared by methods known in the art, for example, see U.S. Pat. No. 3,642,728, incorporated herein by reference.

The most preferred sulfonated polymers for use in the instant invention are sulfonated ethylene/propylene terpolymers which may be prepared by the procedures described in U.S. Pat. No. 3,870,841, incorporated herein by reference.

The sulfonated polymers of the instant invention may be neutralized prior to incorporation into organic solvent or by neutralization of the acid form in situ. For example, preferably the acid derivative is neutralized immediately after preparation. For example, if the sulfonation of an EPDM terpolymer is conducted in solution, then the neutralization of that acid derivative can be conducted immediately following the sulfonation procedure. The neutralized polymer may then be isolated by means well known to those skilled in the art, i.e., coagulation, steam stripping, or solvent evaporation, because the neutralized polymer has sufficient thermal stability to be dried for employment at a later time in the process of the instant invention. It is well known that some unneutralized sulfonic acid derivatives do not possess good thermal stability and the above operations avoid that problem.

The concentration of the neutralized sulfonated polymer in the solvent solution is about 0.1 to about 2.0 weight percent, more preferably about 0.5 to about 6.0 weight percent. As discussed above, a variety of poly-

mer backbones will display the desirable properties discovered in this invention.

Specific examples of organic liquids to be employed as solvents for the polymers include:

Polymer	Organic Liquid
Sulfonated ethylene-propylene terpolymer	aliphatic and aromatic solvent oils such as Solvent "100 Neutral", "150 Neutral", and similar oils; benzene; diesel oil; toluene; xylene; ethyl benzene; pentane; hexane; heptane; octane; isooctane; nonane; decane; and ketone solvents.
sulfonated polystyrene	benzene, toluene, ethyl benzene, methyl ethyl ketone, xylene, styrene, ethylene dichloride, and methylene chloride

In order to reduce the viscosity of the organic hydrocarbon solution of the sulfonated polymer so as to be able to employ the organic hydrocarbon solution in a fluidized bed process, a polar cosolvent may be added to the organic hydrocarbon solution of the sulfonated elastomeric polymer to solubilize the pendant ionic groups. The polar cosolvent will have a solubility parameter of at least 10.0, more preferably at least 11.0, and may comprise from 0.0001 to 15.0 weight percent, preferably 0.001 to 5.0 weight percent, of the total mixture of organic liquid, water insoluble ionic polymer and polar cosolvent.

Normally, the polar cosolvent will be a liquid at room temperature, however, this is not a requirement. It is preferred, but not required, that the polar cosolvent be soluble or miscible with the organic liquid at the levels employed in this invention. The polar cosolvent may be selected from the group consisting of alcohols, amines, di- or tri-functional alcohols, amides, acetamides, phosphates, or lactones and mixtures thereof. Especially preferred polar cosolvents are aliphatic alcohols such as methanol, ethanol, n-propanol, isopropanol, 1,2-propanediol, monoethyl ether of ethylene glycol and n-ethylformamide.

The coating of any solid particulates such as the breaker chemical of fracturing fluid breaker systems can be achieved by spraying a solution of sulfonated ionomer, such as zinc sulfo EPDM terpolymer, onto a cascading stream of granules through an appropriate technique, such as fluidized bed coating. Examples of fluidized bed coating processes are conventional spray coating wherein the solid particulates are coated by spraying the coating solution above or below the bed in a Wurster configuration or a fluidized bed with a rotating bed support plate. It is envisioned that coated solid inorganic or organic breaker systems or other particulates can be utilized in a variety of environmental conditions and yet the release of the breaker or other water soluble component of the breaker can be controlled in such a way that they are available when the reduction of viscosity is needed.

The neutralized sulfonated elastomers of this invention are slowly permeable to water and essentially impermeable to the breaker chemicals mentioned herein under well-bore conditions. Upon introduction into aqueous fracturing fluids or other aqueous wellbore

fluids, the encapsulated substrate slowly absorbs water by diffusion through the polymeric coating. This water dissolves the substrate and sets up an osmotic gradient which in turn draws in more water. Pressure builds up inside the capsule, and it expands until resealable micropores (not pinholes) form in its walls. Concentrated substrate solution is then ejected through the micropores into the surrounding medium. This relieves the pressure inside the capsule which then shrinks. The micropores reseal, and the process repeats itself until insufficient substrate remains for swelling and micropores to form.

Specific examples of preferred breaker chemicals of the instant invention are selected from the group consisting of ammonium and alkali persulfates, alkyl formates, salicylates, acetates, chlorites, phosphates, lactates, chloroacetates, enzymes and other solid breakers. The release of the breakers from the coated solid breaker systems can be controlled by the thickness of the sulfonated polymer coating, the degree of sulfonation of the polymer, the degree of neutralization of the sulfonated groups of the sulfonated polymers, the type of cation in the sulfonated polymers, the biodegradability of the sulfonated polymers, and the intertidity and conformity of application of the polymers.

The thickness of the coating of the neutralized sulfonated elastomeric polymer on the breaker chemical is about 1 to about 100 microns, more preferably about 2 to about 80 microns, and most preferably about 5 to about 70 microns.

The chemical forming the core of the encapsulated breaker chemical may be used per se when it is in the form of a finely divided solid or, in another embodiment of the invention, it may be sprayed as a solution or in liquid form onto small, finely divided seed particles to form a coating on these seed particles. Essentially any solid which is of the proper size and which is inert to the breaker chemical (or other active material) may be used as the seed particle but urea is preferred. This embodiment is especially preferred where the breaker chemical is itself a liquid, or is irregular in shape or not of the proper size.

In another embodiment of this invention, the encapsulated breaker chemical, with or without a seed core, may be further overcoated by processes described above with a solution of thermoplastic polymer material which exhibits permeability properties similar to those of the neutralized elastomer coating overlying the breaker chemical. This overcoat layer is particularly useful in reducing the tackiness of the elastomer layer and thereby allows for the application of a thicker elastomer layer. For example, a sulfonated EPDM elastomer layer may become tacky during the coating process and the coated particles tend to stick together. The application of an overcoat layer of thermoplastic polymer removes the tackiness of the previously coated particles so that thicker layers of the sulfo EPDM coating may be achieved.

Preferred thermoplastic overcoat layers are based on sulfonated styrene polymers or copolymers which are also neutralized to the degree set forth above with respect to the elastomeric polymers. The thickness of the thermoplastic layer is generally less than the thickness of the elastomeric layer, and may range from about 1 to about 20 microns, more preferably from about 1 to about 10 microns, and most preferably from about 1 to about 5 microns.

Thermoplastic polymers which are most preferred as overcoat layers in accordance with this invention include neutralized sulfonated poly-styrene and neutralized sulfonated poly (p-methyl) styrene having a degree of acid neutralization and a molecular weight within the ranges specified above for the elastomeric polymer.

The preferred breaker chemicals which may be encapsulated using the neutralized sulfonated elastomer include ammonium persulfate, sodium persulfate, potassium persulfate, sodium chloride, ammonium bifluoride, ammonium fluoride, sodium fluoride, potassium fluoride, sulfuric acid, citric acid, oxalic acid, ammonium sulfate, sodium acetate and enzymes and mixtures thereof.

The breaker chemical can also be used in combination with a polymeric matrix as described in U.S. Pat. No. 4,738,897 incorporated herein by reference, absorbed on a porous solid such as diatomaceous earth or coated on an inert core substrate such as urea as described above.

Other oil well chemical additives can be encapsulated in addition to or in place of the breaker chemicals. These materials when encapsulated will be administered under the same conditions and in the same ways as in normal use. These oil well chemical additives are selected from the group consisting of: scale inhibitors such as polyacrylates, phosphonates and phosphonic esters; corrosion inhibitor such as acid amine salts, imidazolines and quaternary amines; demulsifiers such as alkoxylated resins, alkoxylated polyols and alkoxylated polyesters; biocides such as glutaraldehydes, isothiazolinones and dithiocarbamates; paraffin inhibitors such as ethylene vinyl acetate copolymers, alpha olefin maleate and fumarate polyesters, and vinyl acetate; foams such as ether sulfates, alpha olefin sulfonates and quaternary amines; cement accelerators such as calcium chloride and aluminum chloride; and gas migration agents such as latex rubbers and aluminum powders.

It is also within the scope of this invention that other inorganic and organic materials may be encapsulated with the polymeric coating system of this invention such as materials used in agricultural applications, wherein these agricultural materials are selected from the group consisting of urea fertilizers, herbicides, pesticides and mixtures thereof.

In order for such elastomeric coatings to be functional, they have to meet one or more of the following criteria: the coating material should show improved barrier properties; the applied thin coating should be a continuous film with few or no defects, i.e., be substantially free of pinholes. The term "pinholes" as used herein is understood to mean discontinuities in the polymeric coating of such size and shape as to prevent osmotic pressure buildup.

Fracture fluids commonly used in fracturing operations include water-based brine fluids containing a water-soluble polymer such as hydroxypropyl guar cross-linked with a transition metal salt as is well known in the art. Other polymers used to viscosify aqueous fracturing fluids are hydroxyethyl cellulose, polyacrylamide, gum karaya and the like. In addition, fracturing fluids may be viscous oils or oil-based emulsions. Viscosification of these is accomplished by addition of surfactants, asphalt, fatty-acid soaps, other emulsion and foam stabilizing agents and the like.

Typical propping agents used in hydraulic fracturing for retaining the integrity of the fractures are nut shells, plastic beads, glass beads, sand, sintered alumina, urea

prills and aluminum spacers. The concentration used depends on the size and shape of the proppant, the type of formation being fractured, the carrying capacity of the fracturing fluids and the desired permeability of the resistant fractures. The concentrations generally range from 1 to 30 lb. per gal.

Other additives commonly used in hydraulic fracturing fluids are fluid loss or wall building agents such as starch, bentonite, silica flour, guar gum and surfactants; friction-reducing agents such as small amounts of high molecular weight linear polymers such as polyacrylamide; specific gravity increasing agents; bactericides; scale-removal/prevention agents, and surfactants or alcohol to reduce interfacial tension and the resistance to return flow.

The following Examples are illustrative of the invention.

EXAMPLE 1

This example sets forth the preparation of two sulfonated EPDM terpolymers which are subsequently neutralized to form the zinc salt (SEFDM).

Sulfonated EPDM terpolymers are prepared by sulfonating a terpolymer comprising about 50 weight percent ethylene, about 5 weight percent ethylenedine norbornene (ENB) and the balance being propylene. This material is available from Uniroyal under the trademark "ROYALENE" 521. Sulfonation was carried out by treatment with acetyl sulfate and neutralization with Zn (Ac)₂ according to the procedure of U.S. Pat. No. 3,836,511, herein incorporated by reference.

Two species of neutralized elastomer were produced, one having 10 meq. of zinc sulfonate groups per 100 grams of the EPDM terpolymer (hereinafter designated ZSE-10), and the other having 25 meq. of zinc sulfonate groups per 100 grams of the EPDM terpolymer (hereinafter designated ZSE-25).

EXAMPLE 2

Improved Barrier Properties of a Sulfonated Polymer

A solution of a zinc neutralized sulfonated EPDM polymer was prepared for application as a coating solution. The solution cast coating was applied over urea samples in order to measure the barrier properties for urea extraction by water through the thin film coating.

Solution A was prepared by mixing 2.5 grams of a zinc sulfo-EPDM similar to the one described in Example 1 (Uniroyal Ionic Elastomer 2560), containing 25 meq. of sulfonate groups per 100 grams of ethylene propylene ethylenenorbornene terpolymer, neutralized with zinc, in 100 grams of a solvent consisting of 97.5% toluene and 2.5% methanol reagent.

To determine the barrier properties of films formed from the solution of the sulfonated EPDM terpolymer, urea slides were coated for immersion tests. The procedures for preparing coated samples of urea slides and conduction immersion tests are described as follows:

Urea samples were prepared by depositing reagent grade urea (Fischer Scientific) over microscope glass slides. This was done by dipping glass slides into molten urea at a temperature of about 135°-145° C., followed by cooling and solidification of the urea layer. The urea layer was built up to about 7 mm. by 4 to 5 successive dipping and cooling cycles. These urea samples were then coated by a polymeric film using a second dipping procedure. Urea slides were repeatedly dipped into polymeric solutions such as those described above, fol-

lowed by drying in a vacuum oven at 70° C. for about 3 hours. The dipping and drying cycles were repeated until the film thicknesses shown in Table I were obtained.

The barrier properties of the various polymeric films were determined by immersion of each coated urea slide in about 100 g. of deionized water at room temperature. The amount of urea released into the water was determined by recovering the urea after evaporating the water. Each sample was initially immersed for 1 day, followed by immersion in fresh water for 3 days and for weekly intervals thereafter.

Table I shows the permeabilities of urea solutions extracted from the coated urea slides and immersed in water at room temperature. The permeabilities of the coating materials were determined by applying Fick's law of diffusion at steady state. Fick's law states that:

$$J_m = DA \frac{C}{X}$$

TABLE I
PERMEABILITY OF UREA SOLUTION FROM
COATED UREA SLIDES IN WATER AT ROOM
TEMPERATURE

Sample No.	Coating Material	Ratio wt/wt	Film Thickness Microns	Permeability (P = DK) cm ² /sec.
141-3	Tung Oil	—	75	4.3×10^{-9}
141-6	Tung Oil	—	125	7.6×10^{-9}
158-4	Polyurethane	—	100	1.3×10^{-9}
158-5	Polyurethane	—	40	2.1×10^{-9}
28-14	ZSE-25	—	10	9.6×10^{-11}
84-1	ZSE-25	—	25	8.6×10^{-11}
84-2	ZSE-25	—	30	8.6×10^{-11}

where J_m = mass flux (loss) through the film or membrane, A = transport area, C = concentration gradient, X = film or membrane thickness, and D = membrane diffusivity constant which is equal to the ratio of permeability (P) over the solubility ratio (K) of urea in the membrane and in water.

The performance of the zinc-sulfo-EPDM film was compared with that formed from solutions of other commercial coating materials. The first commercial coating solution was a tung oil solution made by Formby of Mississippi at 30 weight percent solids in petroleum distillate. The second commercial coating solution was lined oil modified polyurethane Type I made by Minwax Paint Co. of New Jersey at 45% solids in petroleum distillate. The two commercial coatings were cured at 70° C. for 48 hours after coating.

The permeability of urea solutions through the zinc sulfonated EPDM terpolymer film was found to be about 3 orders of magnitude lower than either that of tung oil or that of polyurethane. The use of tung oil and polyurethane as release control coatings on water soluble fertilizers is disclosed in U.S. Pat. Nos. 3,321,298 and 3,223,518.

The present Example shows that thin films of zinc sulfonated EPDM terpolymer complex provide a much better barrier than do commercial materials.

EXAMPLE 3

In this Example, thick coatings of reagent sulfur and paraffin wax (M.P. = 55° C.) were applied through melting (i.e., these materials were melted at about 5° C. to 10° C. above their melting point and then after quickly dipping urea samples in the melt, the hot coated sample

was brought to room temperature slowly). This layering procedure was repeated three to four times to obtain a thick coating. Both unsulfonated EPDM and PEVAC (a copolymer of ethylene and vinyl acetate containing about 60 weight percent ethylene) were applied from 2.5% polymer solutions in the same solvent as the solvent for the sulfo EPDM.

FIG. 1 shows that ZSE-10 offered the best protection preventing the dissolution of urea in water at room temperature (about 22° C.). Uncoated urea dissolved quickly in water, but even thick coatings of sulfur, unsulfonated EPDM and PEVAC on similar samples did not sufficiently protect urea from dissolving in water. Paraffin wax and modified polyurethane Type I (made by Minwax Paint Company) protected urea from dissolving in water for at least six days. ZSE-10, however, performed the best in protecting urea from water dissolution.

EXAMPLE 4

Fluidized Bed Process for SEPDM Coating

SEPDM coated sodium persulfate granules were produced using the following procedure:

4 kg of 20-30 mesh sodium persulfate were introduced into a fluid bed coating machine, including a Wurster insert, manufactured by Glat Air Techniques Inc., model number GPCG-5. The sodium persulfate bed was fluidized by blowing 130 scfm of heated air (45° C.) through bed. After the bed reached a temperature of 30° C., a 1.25 weight percent solution of the SEPDM polymer in toluene and methanol cosolvent was sprayed onto the sodium persulfate granules at the Wurster insert entrance. The spray nozzle used was a commercial two fluid nozzle using air at 3 bars pressure to form an atomized spray regime in the Wurster insert.

The spraying was continued at 40 gm/min rate until the required thickness of polymeric coating was built up on the sodium persulfate, i.e., approximately 80 minutes per a coating level of 1 weight percent polymer on the sodium persulfate.

After the solution was sprayed onto the granules in the Wurster insert, the thus coated granules were blown by the heated air upwards into the drying section of the machine. Here, the solvents were evaporated by the hot stream, leaving a thin coat of dried polymeric material on the granules. The dried granules fell back into the fluid bed and then re-entered the Wurster insert where the coating process was repeated. Thus, multiple films or layers of the sulfonated polymeric coating was built up until the spraying was stopped.

After a 1 weight % coating was put on the granules, a 60 gram sample was taken and marked as 1 wt % of SEPDM on sodium persulfate. The spraying was continued until 2 wt % SEPDM was added. The spraying was then stopped and the coated granules were dried with the hot air for 5 minutes.

EXAMPLE 5

2.34 grams of 20 to 30 mesh granulated sodium persulfate coated with 1 and 2 weight percent SEPDM terpolymer as set forth in Example 4, were placed in 30 grams of a 30 weight percent barium chloride solution. The sodium persulfate converts to approximately 5.5 grams of barium sulfate, as shown by the uncoated persulfate data at 250° F./121° C. The coated solids, after remaining at the desired release temperature and time, were separated from the finer barium sulfate solids

and the water by pouring through a 40 mesh sieve. The sieve was thoroughly rinsed with water to remove any solids or liquids clinging to coated solids. The barium sulfate in water plus any water soluble salts were left overnight to separate. The free water was then decanted from the solid barium sulfate. The remaining water was removed by drying in an oven at 150° F. (65° C.) overnight. The remaining barium sulfate was weighed and recorded in Table II. The percent sodium persulfate released in given by using the uncoated 10 weight at 100% released.

TABLE II

Release of Coated Sodium Persulfate in Water at Time and Temperature

Coated Sodium Persulfate	Temperature (°F./°C.)	Release of Coated Sodium Persulfate by Weight in grams of Converted Barium Sulfate and by Percent versus Time in hours			
		4		8	
		weight (g)	%	weight (g)	%
Sodium Persulfate Uncoated	75/24	0.88	100	0.82	100
	150/65	4.51	100	4.02	100
	250/121	5.17	100	5.43	100
Sodium Persulfate Plus 1 weight Percent S-EPDM Coating	75/24	0.26	30	0.60	73
	150/65	1.19	26	1.76	44
	250/121	4.53	88	4.46	82
Sodium Persulfate Plus 2 weight Percent S-EPDM Coating	75/24	0.20	23	0.38	46
	150/65	1.03	23	1.76	44
	250/121	4.48	87	4.37	80
Sodium Persulfate Plus 2 weight percent S-EPDM plus 1 weight percent SPS	75/24	0.22	25	0.40	49
	150/65	1.12	25	1.66	41
	250/121	4.06	79	4.38	81

EXAMPLE 6

The following Example illustrates the preparation of a sodium sulfonated polystyrene thermoplastic polymer (SPS) which may be used as an additional layer over the SEPDM layer.

Sulfonated polystyrene is manufactured as a 30% suspension/emulsion in water. The monomers of sodium styrene sulfonate (NaSS) and styrene are added to water (oxygen free) containing surfactant (sodium lauryl sulfate), catalysts (potassium persulfate and sodium bisulfate) and chelates (EDTA) for iron. The mixture is reacted at 180° F. (82° C.) for 3 hours. After the reaction is complete, an antioxidant (BHT) is added. The final product is 30% SPS suspended/emulsified into water. The polymer is oil soluble since only 3.8% NaSS is present in the polymer.

EXAMPLE 7

The multilayer coating with sulfonated polystyrene polymer is achieved by spraying the sodium sulfonated polystyrene (SPS), as prepared in Example 6 or a dilution thereof, onto the cascading stream of granules coated as described above with the sulfonated EPDM terpolymer. The SPS polymer is a suspension/emulsion in water so it can easily be diluted with water to the proper level for spraying multilayer coats.

After 2 wt % of SEPDM was put on the sodium persulfate as set forth in Example 4, a 1/2 wt. % of SPS was added as a top layer. The conditions were kept the same as in Example 4 above except that a 5 wt. % SPS solution, a dilution of 30 wt. % SPS solution in water, was sprayed onto a rate of 40 gm/min. After approximately 9 minutes, a 1/2 wt. % SPS coating was completed. The spraying was stopped and the product was dried with hot air

another 5 minutes. The product comprised 2 wt. % SEPDM plus 1/2 wt. % SPS on sodium persulfate.

The release properties of this material were also evaluated as in Example 5 above and are reported as the last entry in Table II.

EXAMPLE 8

Sodium persulfate was layered/coated on urea seed granules by using the following procedure: 1.6 kg of 2.5 mm OD urea granules were introduced into a fluid bed coating machine with a 2 liter bowl, manufactured by

Glatt Air Techniques Inc., model number GPCG-1. The urea bed was fluidized by blowing approximately 130 scfm of heated air (45° C.) through the bed. After the bed reached 30° C., a 10wt % sodium persulfate solution in water and methanol was sprayed onto the urea fluidized to the top of the bowl with a top spray nozzle. The spray nozzle used was a commercial two-fluid nozzle using air at 2 bars pressure to form an atomized spray regime in the bowl.

The spraying was done at 20 gm/min and continued until approximately a 5 wt % coating of sodium persulfate was added. The spraying took approximately 40 minutes to add the 5 wt % level. The product was urea particles coated with 5 wt % sodium persulfate.

These coated seed particles may be further coated with the elastomer and elastomer/thermoplastic combination as set forth above.

EXAMPLE 9

Fluidized Bed Process

Multilayer Coating of SEPDM and SPS

SEPDM and SPS multilayer coated sulfamic acid granules were produced using the following procedure:

Six kilograms of 20-30 mesh sulfamic acid were introduced into a fluid bed coating machine, including a Wurster insert, manufactured by Glatt Air Techniques Inc., Model number GPCG-5. The sulfamic acid was fluidized by blowing 130 scfm heated air (55° C.) through the bed. After the bed reached a temperature 40° C., a 1.25 weight percent solution of the SEPDM polymer in toluene and methanol cosolvent was sprayed onto the sulfamic acid granules at the Wurster insert entrance. The spray nozzle used was a commer-

cial two fluid nozzle using air at 3 bars pressure to form an atomized spray regime in the Wurster insert.

layer (outer layer) is given in first column in Table III.

TABLE III
RELEASE OF COATED SULFAMIC ACID

Coated Sulfamic Acid Sample (amount/type of coating)	Weight Percent of Sulfamic Acid Released into Water from Coated Sample as a Function of Time and Temperature							
	4 Hours		8 hours		16 hours			
	75° F.	150° F.	250° F.	75° F.	150° F.	250° F.	75° F.	150° F.
Uncoated	100	100	100	100	100	100	100	100
1.5 wt. % Z-SE	100	100	100	92	100	100	100	100
1.5 wt. % Z-SE + 0.5 wt. % SPS	82	100	100	100	100	100	100	100
(SPS Top)								
3 wt. % Z-SE + 0.5 wt. % SPS	53	100	98	76	97	100	92	100
(Z-SE Top)								
3 wt. % Z-SE + 1 wt. % SPS	45	100	100	66	100	100	95	100
(SPS Top)								
4 wt. % Z-SE + 1 wt. % SPS	26	91	100	42	93	99	69	100
(Z-SE Top)								
4 wt. % Z-SE + 1.5 wt. % SPS	28	71	99	62	97	99	70	100
(SPS Top)								
5 wt. % Z-SE + 2 wt. % SPS	25	62	83	36	89	78	61	97
(SPS Top)								
6 wt. % Z-SE + 2 wt. % SPS	14	40	59	16	62	99	26	84
(Z-SE Top)								
6 wt. % Z-SE + 2.5 wt. % SPS	16	40	71	24	64	100	41	88
(SPS Top)								

Note:
Z-SE is Zn sulfo EPDM sprayed a 1.25 wt. % polymer solution in toluene/methanol at 97/3 weight ratio.
SPS is Na sulfo polystyrene sprayed from a 5 wt. % polymer water external emulsion.

The spraying was continued at a 40 gm/minute rate until the required amount of polymeric coating was built up on the sulfamic acid, i.e., approximately 120 minutes for a coating level of 1 wt. % polymer on the sulfamic acid.

After the solution was sprayed on the granules in the Wurster insert, the thus coated granules were blown by the heated air upwards into the drying section of the machine. Here, the solvents were evaporated by the hot stream, leaving a thin coat of dried polymeric material on the granules. The dried granules fell back into the fluid bed and then re-entered the Wurster insert where the coating process was repeated. Thus, multiple films or layers of the sulfonated polymeric coating were built up until the spraying was stopped.

After a 1.5 wt. % coating of SEPDM was on the granules, a sample was taken and marked 1.5 wt. % SEPDM on sulfamic acid.

The remaining 1.5 wt. % coated sulfamic acid was then coated with 1 wt. % of SPS as a top layer to prevent agglomeration of particles and allow the build up of multilayers of SEPDM and SPS. The conditions were kept the same as above except a 5 wt. % SPS solution, a dilution of 30 wt. % SPS solution in water, was sprayed onto the 1.5 wt. % SEPDM coated sulfamic acid at a rate of 40 gm/min. After approximately 9 minutes the 1 wt. % SPS coating was completed. The spraying was stopped and the product dried with hot air another 5 minutes. A sample was taken marked 1.5 wt. % SEPDM plus 1 wt. % SPS on sulfamic acid.

The process was continued and samples taken with varying multilayers of SEPDM and SPS until a total of 6 wt. % SEPDM and 2.5 wt. % SPS were sprayed in layers on the sulfamic acid. The amount and type of each coated sulfamic acid sample as well as the top

EXAMPLE 10

Coated 20 to 30 mesh granulated sulfamic acid samples with the multilayer coating reported above in Example 9 and in Table III were placed in water for release studies. 2.0 grams of coated sulfamic acid samples were placed in 20 grams of deionized water.

The coated solids, after remaining at the desired release temperature and time, were separated from the water containing the released sulfamic acid by pouring the solid plus water through a 100 mesh sieve. The sieve was thoroughly rinsed with water to remove any released sulfamic acid clinging to the coated solids. The water was then evaporated in the oven at 75° C. The percent of sulfamic acid released for each coating level is given in Table III.

EXAMPLE 11

A viscous (gelled) 2 weight percent potassium chlorate solution was used to test the effects of coated breaker chemical (oxidizer) on reducing the viscosity or breaking the gel of the viscous brine solution. The coated breaker was compared with the base gel without breaker and with the uncoated oxidizer added to the base gel.

The viscous brine was made by adding 50 pounds per 1000 gallons of hydroxypropyl guar (HPG) to a 2 wt % KCl solution.

The viscosities were measured with a Fann 35 VG viscometer at 311 sec⁻¹ (300 rpm) shear. Viscosities were taken during heatup to 175° F. (79.4° C.) and versus time at 175° F. Two hundred milliliters of gelled brine was used for the tests. The coated breaker sodium

persulfate at 8 and 4 pounds per 1000 gallons (PPT) of gelled brine were added to the Fann 35 VG meter measuring cup. Also 0.5 PPT of uncoated sodium persulfate were added in one test to show the effect of the SEPDM/SPS coatings on the release of sodium persulfate with time at 175° F. The base gelled brine with no additives were measured for comparisons.

Table IV shows the advantage of coating the sodium persulfate to delay the release of the oxidizer at a temperature of 175° F.

The uncoated sodium persulfate broke the gel to 5 cp in 30 minutes whereas the coated sodium persulfate at 4 and 8 PPT were only 14 and 8 cp after 160 minutes. Comparison with the untreated base gel shows the oxidizers all break the gel.

The film forming properties of sulfonated polymers permits them to be used in coating applications, including controlled release products in oil and gas well operations (e.g., controlled release fracturing fluid breaker system or "breakers").

TABLE IV

EFFECT OF COATED OXIDIZER (SODIUM PERSULFATE) ON VISCOSITY OF HYDROXYPROPYL GUAR (HPG) GELLED 2% POTASSIUM CHLORIDE (KCL) SOLUTION

- Viscous brine made by adding 50 pounds per 1000 gallons (PPT) of HPG to 2% KCl solution (0.6 g HPG per 100 ml solution).
- Viscosities measured with Fann 35 VG viscometer at 311 sec⁻¹ (300 rpm).
- Viscosities taken during heatup to 175° F. and versus time at 175° F.
- Two hundred milliliters of gel treated with oxidizer for tests.

Viscosity (cp) of Gelled Solution with Oxidizers - Normalized*					
Temperature (°F.)	Time (min)	No Oxidizer	Coated Oxidizer #2 (8 ppt)	Coated Oxidizer #2 (4 ppt)	Uncoated Na ₂ S ₂ O ₈ (3 ppt)
80		50.0	50.0	50.0	50.0
100		47.2	46.3	47.5	47.0
120		43.4	42.6	44.1	43.1
140		39.2	—	38.2	37.6
160		33.5	—	33.3	31.7
175	0	30.2	28.9	29.2	28.2
	5	29.2	28.4	29.9	18.3
	10	29.2	28.4	29.9	13.4
	20	30.2	26.8	28.9	7.9
	30	30.2	24.2	27.9	5.4
	40	30.2	22.1	25.5	
	60	30.2	18.4	22.5	
	80	30.2	15.8	19.6	
	100	30.2	14.7	17.6	

TABLE IV-continued

EFFECT OF COATED OXIDIZER (SODIUM PERSULFATE) ON VISCOSITY OF HYDROXYPROPYL GUAR (HPG) GELLED 2% POTASSIUM CHLORIDE (KCL) SOLUTION

160	30.2	7.9	13.7
Coated Oxidizer #1 (LAM 2J) Urea = 83.4%, Persulfate = 9.0%, S-EPDM = 3.1% & SPS = 2.5%			
Coated Oxidizer #3 (Lam 10G) Persulfate = 82.0%, Urea = 4.3%, S-EPDM = 2.0%, SPS = 3.0%			
*Normalized to 50 cp at 80° F.			

Coatings of neutralized sulfonated polymers on breaker chemicals which are used in fracturing fluids will act as barriers to water soluble components of the fracturing fluid thereby shielding the breaker chemical from the premature release of the breaker chemical into the fracturing fluid.

Because of their unique barrier properties sulfonated polymers can be used to make cost effective controlled release breaker chemicals. The benefits obtained by the use of these coatings can include labor savings, increased breaker utilization efficiency, time savings and reduction in residual damage to the well caused by residual gels.

What is claimed is:

1. An encapsulated particulate composition comprising:

- a solid particulate substrate;
- a coating substantially free of pinholes comprising a neutralized sulfonated elastomeric polymer having a thickness of at least about 1 micron deposited on the surface of particles of said substrate, wherein said neutralized sulfonated polymer encapsulates said substrate, wherein said neutralized sulfonated polymer is permeable to said substrate at conditions of use and said neutralized sulfonated polymer is non-reactive to said substrate, and
- a layer of thermoplastic polymer overcoating said coating.

2. The composition of claim 1 wherein said thermoplastic polymer is a neutralized sulfonated styrene polymer.

3. The composition of claim 2 wherein the thickness of said layer of thermoplastic polymer is within the range of from about 1 to about 20 microns.

4. The composition of claim 1 wherein said elastomeric polymer is a neutralized sulfonated EPDM terpolymer.

5. The composition of claim 1 wherein said substrate is selected from the class consisting of herbicides, fertilizers and pesticides.

6. The composition of claim 5 wherein said substrate is urea.

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US006669771B2

(12) **United States Patent**
Tokiwa et al.(10) **Patent No.:** **US 6,669,771 B2**
(45) **Date of Patent:** **Dec. 30, 2003**(54) **BIODEGRADABLE RESIN COMPOSITIONS**(75) **Inventors:** **Yutaka Tokiwa, Tsukuba (JP); Akihito Tsuchiya, Shiga (JP)**(73) **Assignees:** **National Institute of Advanced Industrial Science and Technology, Tokyo (JP); Allmighty Co., Ltd., Hyogo (JP); Yukata Tokiwa, Ibaraki (JP)**(*) **Notice:** **Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.**(21) **Appl. No.:** **10/149,276**(22) **PCT Filed:** **Dec. 8, 2000**(86) **PCT No.:** **PCT/JP00/08725**§ 371 (c)(1),
(2), (4) **Date:** **Sep. 13, 2002**(87) **PCT Pub. No.:** **WO01/42367****PCT Pub. Date:** **Jun. 14, 2001**(65) **Prior Publication Data****US 2003/0079654 A1 May 1, 2003**(30) **Foreign Application Priority Data****Dec. 8, 1999 (JP) 11/349437**(51) **Int. Cl.⁷ C08L 101/16; C08L 5/14; C08L 67/00**(52) **U.S. Cl. 106/162.7; 106/15.05; 106/16; 106/162.1; 106/205.01; 264/330; 264/331.11; 424/78.09; 523/122; 524/27; 524/55; 524/56**(58) **Field of Search 106/162.1, 162.7, 106/205.01, 15.05, 16; 524/27, 55, 56; 264/330, 331.11; 523/122; 424/78.09**(56) **References Cited****U.S. PATENT DOCUMENTS****5,532,350 A 7/1996 Cottrell et al. 536/76****5,545,485 A * 8/1996 Hashitani et al. 428/423.1**
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Primary Examiner—Anthony J. Green**(74) Attorney, Agent, or Firm—Knobbe, Martens, Olson & Bear LLP**(57) **ABSTRACT**

The present invention provides a biodegradable resin composition with improved biodegradability or with an additional useful function (antibacterial properties), while maintaining the mechanical properties of the biodegradable resin. More specifically, the present invention provides a biodegradable resin composition containing a biodegradable resin such as a polylactic acid polymer and a mammalian digestion product such as a mannanoligosaccharide. The present invention further provides various biodegradable products produced by molding this biodegradable resin composition into desired shapes.

14 Claims, No Drawings

BIODEGRADABLE RESIN COMPOSITIONS

This application is the U.S. National Phase under 35 U.S.C. §371 of International Application PCT/IP00/08725, filed Dec. 8, 2000, which claims priority to Japanese Patent Application No. 11/349437, filed Dec. 8, 1999. The International Application was not published under PCT Article 21(2) in English.

TECHNICAL FIELD

The present invention relates to biodegradable resin compositions. More specifically, the present invention relates to a biodegradable resin composition that can be produced at reduced cost while maintaining the strength and physical properties of the biodegradable resin; a biodegradable resin composition with improved biodegradability; and a resin composition having an additional useful function.

BACKGROUND ART

Plastics have conventionally been used in a wide variety of fields because they are lightweight, durable and excellent in molding processability. On the other hand, however, plastics decompose very little under natural environmental conditions. Therefore, if disposed of by underground burial, plastics remain almost permanently. If plastics are disposed of by incineration, problems arise such as the generation of toxic gas or damage to the incinerator. The disposal of plastics has been focused on as an environmental problem.

Therefore, with the purpose of protecting the global environment, there have been active attempts to develop biodegradable resins. Biodegradable resins are currently classified into the following groups:

chemically synthesized resins such as polycaprolactone, polylactic acid, polyvinyl alcohol, polybutylene succinate and copolymers thereof;

microbially produced resins such as polyhydroxybutyrate/valerate copolymers; and

natural product-derived resins such as acetyl cellulose.

Further, there is a proposal to add starch or processed starch to these resins in order to reduce the cost and improve biodegradability (Japanese Unexamined Patent Publications Nos. 14228/1990, 31333/1991, 248851/1992, 331315/1993 and 207047/1994).

The addition of starch, etc. to biodegradable resin improves biodegradability but severely reduces strength, elongation (%) and like mechanical properties required of the resin composition and moldings thereof, thus causing the problem that the resulting products become fragile. Therefore, in reality, there is a limitation on the proportion of starch to resin and the desired cost reduction has not yet been achieved.

DISCLOSURE OF INVENTION

An object of the present invention is to provide a biodegradable resin composition with improved biodegradability while substantially maintaining the mechanical properties of the biodegradable resin. Another object of the invention is to provide a biodegradable resin composition that can be produced at reduced cost while substantially maintaining the mechanical properties of the biodegradable resin. A further object of the invention is to provide a biodegradable resin composition with an additional useful function while substantially maintaining the mechanical properties of the biodegradable resin.

The present inventors carried out intensive research day and night to achieve the above objects and found that the

addition of a mannan digestion product to a biodegradable resin can provide a resin composition with improved biodegradability and furthermore can produce the resin composition and moldings thereof at a lower cost than the single use of biodegradable resin while the mechanical properties of the resin composition and moldings thereof are substantially equivalent to those of the biodegradable resin and moldings thereof. The inventors further found the following specific effect of the resin composition comprising a biodegradable resin and a mannan digestion product: the resin composition can adsorb bacteria to different degrees depending on the mannan digestion product content of the resin composition. The inventors confirmed that various products with antimicrobial barrier properties can be produced by using the above-mentioned resin composition. The bacterial adsorption or adhesion peculiar to the resin composition of the invention is presumably one of the causes of the excellent biodegradability of the resin composition of the invention. The present invention has been developed based on these novel findings. More specifically, the invention provides the following biodegradable resin compositions:

Item 1. A biodegradable resin composition comprising a biodegradable resin and a mannan digestion product.

Item 2. The biodegradable resin composition according to item 1 wherein the biodegradable resin is an aliphatic polyester.

Item 3. The biodegradable resin composition according to item 1 wherein the biodegradable resin is at least one member selected from the group consisting of polyhydroxybutyrate, polylactic acid, polycaprolactone, polybutylene succinate, polybutylene succinate/adipate, polybutylene succinate carbonate, polyvinyl alcohol and cellulose acetate.

Item 4. The biodegradable resin composition according to item 1 wherein the biodegradable resin is a polylactic acid polymer.

Item 5. The biodegradable resin composition according to item 4 wherein the polylactic acid polymer is a homopolymer or copolymer of lactic acid (polylactic acid), or at least one copolymer of lactic acid and at least one member selected from the group consisting of cyclic lactone, glycolic acid, α -hydroxybutyric acid, α -hydroxyisobutyric acid, α -hydroxyvaleric acid, hydroxypentanoic acid, hydroxycaproic acid, hydroxyheptanoic acid, hydroxyoctanoic acid, ethylene glycol, polyethylene glycol, 1,4-butanediol, succinic acid and sebacic acid.

Item 6. The biodegradable resin composition according to item 1 wherein the biodegradable resin is a polylactic acid.

Item 7. The biodegradable resin composition according to item 1 wherein the biodegradable resin has a number average molecular weight of 20,000 or more and a melting point of 70° C. or higher.

Item 8. The biodegradable resin composition according to item 1 wherein the mannan digestion product is at least one member selected from the group consisting of mannooligosaccharides, galactomannan digestion products and glucomannan digestion products.

Item 9. The biodegradable resin composition according to item 1 wherein the proportion of the mannan digestion product is 0.05 to 40 wt. % relative to 100 wt. % of the biodegradable resin.

Item 10. The biodegradable resin composition according to item 1 wherein the proportion of the mannan digestion product is 1 to 40 wt. % relative to 100 wt. % of the biodegradable resin.

Item 11. The biodegradable resin composition according to item 1 which further comprises a crystal nucleating agent.
 Item 12. The biodegradable resin composition according to item 11 wherein the crystal nucleating agent is at least one member selected from the group consisting of tale, boron nitride, calcium carbonate, magnesium carbonate and titanium oxide.

The present invention further provides moldings produced by molding the above biodegradable resin compositions. Such moldings include, for example, biodegradable products and products with antimicrobial barrier properties.

BEST MODE FOR CARRYING OUT THE INVENTION

The mannan digestion product used in the present invention is a compound formed by the digestion of mannan and comprising mannose.

Mannans are polysaccharides mainly consisting of mannose and include those classified into the following classes:

- (1) Plant-derived mannans: such mannans include copra meal and flakes from coconut palms, Heacra Palm (a plant of the palm family originating in South Africa), tsukunimo (a type of yam) mannan, and yamaimo (Japanese yam) mannan.
- (2) Glucomannans: polysaccharides comprising glucose and mannose. Such mannans include, for example, mannans from konjac tubers, lily, narcissus and the subterranean stem of *Lycoris radiata*.
- (3) Galactomannans: polysaccharides comprising galactose and mannose. Such mannans include, for example, mannans from locust bean gum, soybean hulls derived from soybean seed coat, jimson gum, tara gum, guar gum, etc.
- (4) Other mannans: mannans composed of mannose and at least two other sugars. Such mannans include D-galacto-D-glucosyl-mannan contained in the wood of conifers, and mannan from xanthan gum, etc.

The mannan digestion product used in the present invention can be obtained by digesting various mannans, including those exemplified above, using a suitable method. For example, the following mannan digestion methods are known: biochemical digestion methods directly using polysaccharide-digesting enzymes (mannanase, galactomannanase, gluco-mannanase, etc.) or bacteria producing such enzymes; chemical digestion methods using acids or alkalis; and physical digestion methods using high speed stirrers or shearers. A wide variety of mannan digestion products obtained by the above digestion methods can be used in the present invention. The mannan digestion product used in the present invention may be obtained by any of the above digestion methods. However, the mannan digestion product production method is not limited thereto.

The mannan digestion product includes, for example, β -1,4 mannosidase, β -1,4 mannotriose, β -1,4 mannotetraose, methyl β -mannoside and like β -1,4 mannooligosaccharides; β -1,6 galactomannooligosaccharide, β -1,4 galactomannooligosaccharide, α -1,6 galactomannooligosaccharide, α -1,3 galactomannooligosaccharide and like mannooligosaccharides in which one or two galactoses are bonded to β -1,4 mannosidase, β -1,4 mannotriose or β -1,4 mannotetraose to form branched structure; galactomannan digestion products such as oligosaccharides obtained by digestion of copra lees, coffee lees, guar gum or locust bean gum with mannanase; oligosaccharides wherein glucose or maltose is bonded via a β -1,4 bond

to mannotriose, mannotetraose or the like; and glucomannan digestion products contained in konjac.

For the sake of convenience, commercially available mannan digestion products may be used in the present invention. Alternatively, for example, galactomannan digestion products can be obtained by extracting galactomannan from the seeds of locust, tara or guar plants by water extraction or alcohol precipitation and then digesting the galactomannan with an acid or an enzyme such as galactomannanase and isolating the fraction with a molecular weight of 5,000 to 50,000, preferably 10,000 to 20,000. It is also possible to produce glucomannan digestion products by swelling konjac powder with water to produce a konjac paste and digesting the konjac paste with glucomannanase. These mannan digestion products may be purified or roughly purified products and can be formed into any desired shapes, for examples, aqueous solutions, gels and like liquids, semi-liquids, powders, granules and like solids, or dried products.

It is also possible to use mannan digestion product derivatives as mannan digestion products in the invention. Mannan digestion product derivative means a wide variety of compounds produced by a dehydration condensation reaction for forming a chemical bond between the hemiacetal hydroxyl group of a mannan digestion product and other substance. The other substance bound to the hemiacetal hydroxyl group includes, for example, ribose, ascorbic acid, acrylic acid, styrene, higher alcohols and derivatives thereof, and aliphatic ethers, long-chain epoxy derivatives and the like. Examples of useful mannan digestion product derivatives include isopropylidene derivatives, benzylidene derivatives, butylene glycol derivatives, polyalcohol derivatives and pyridolone derivatives.

The biodegradable resin used in the present invention means a resin (plastic) digested by the action of microorganisms or enzymes existing in nature such as the soil or sea. Any known biodegradable resin may be used as the biodegradable resin. Useful resins include, for example, microbially produced resins, natural high molecular weight resins, synthesized high molecular weight resins and natural-synthetic polymer composite resins. Specific examples include aliphatic polyesters such as polycaprolactone, polylactic acid, polyhydroxybutyrate/valerate; polyvinyl alcohols, acetyl cellulose, methyl cellulose, ethyl cellulose, poly- β -hydroxybutyric acid and copolymers thereof; polybutylene succinate and copolymers thereof; and a starch-caprolactone complex.

Aliphatic polyesters and polyvinyl alcohols are preferred. Especially preferred are aliphatic polyesters, which are comparatively low-cost thermoplastic resins with excellent heat resistance and can be melted and molded.

Prototype and commercially available biodegradable plastics composed of polyvinyl alcohols include, for example, "Poval" (trade name, product of Kuraray Co., Ltd.).

Examples of aliphatic polyesters include polyester resins such as a resin comprising 3-hydroxybutyric acid homopolymer or a copolymer of 3-hydroxybutyric acid and other hydroxy fatty acid; polylactic acid resins, polycaprolactone resins, and aliphatic polyesters mainly consisting of glycol and an aliphatic dicarboxylic acid or an anhydride thereof. Prototype and commercially available aliphatic polyester resins include, for example, the resins known by the trade name "Biopol" (polyhydroxybutyrate/hydroxyvalerate copolymer, product of Monsanto Japan, Ltd.), the trade name "Lacea" (polylactic acid, product of Mitsui Chemicals, Inc.), the trade name "Lacty" (polylactic acid, product of

Shimadzu Corporation), the trade name "EcoPLA" (polylactic acid, product of Cargill Dow Polymers, LLC), the trade name "Lupec" (polybutylene succinate carbonate, product of Mitsubishi Gas Chemical Company, Inc.), the trade name "Lunare SE" (polyethylene succinate, product of Nippon Shokubai Co., Ltd.), the trade name "Bionolle #1000" (polybutylene succinate, product of Showa Highpolymer Co., Ltd.), the trade name "Bionolle #3000" (polybutylene succinate/adipate copolymer, product of Showa Highpolymer Co., Ltd.), and the trade names "Celgreen PH" and "Celgreen P-HB" (polycaprolactones, products of Daicel Chemical Industries, Ltd.).

Also usable are blends prepared by mixing these aliphatic polyesters and starch. Commercially available blend products include, for example, "Mater-Bi" manufactured by The Nippon Synthetic Chemical Industry Co., Ltd. and "Novon" manufactured by Chisso Corporation. The resins mentioned above may be used in mixtures of two or more.

Of these aliphatic polyesters, especially preferred are aliphatic polyesters consisting chiefly of glycol and an aliphatic dicarboxylic acid or an anhydride thereof, and polylactic acid polymers.

Examples of useful glycols include ethylene glycol, 1,4-butanediol, 1,8-hexanediol, decamethylene glycol, neopentylglycol and 1,4-cyclohexane dimethanol. These glycols may be used in combinations of two or more. Examples of aliphatic carboxylic acids (or anhydrides thereof) include succinic acid, adipic acid, suberic acid, sebacic acid, dodecanoic acid, succinic anhydride and anhydrous adipic acid. These acids may be used in combinations of two or more. Useful aliphatic polyesters further include high molecular weight aliphatic polyesters produced by a coupling reaction using diisocyanate, oxazoline, diepoxy compounds or other coupling agents.

Examples of polylactic acid polymers include homopolymers or copolymers comprising lactic acid as a monomer component (polylactic acids), copolymers of lactic acid and one or more kinds of compounds selected from: cyclic lactones such as ϵ -caprolactone; oxyacids such as glycolic acid, α -hydroxybutyric acid, α -hydroxyisobutyric acid, α -hydroxyvaleric acid, hydroxypentanoic acid, hydroxyhexanoic acid, hydroxyheptanoic acid and hydroxyoctanoic acid; glycols such as ethylene glycol, polyethylene glycol and 1,4-butanediol; dicarboxylic acids such as succinic acid and sebacic acid. Random copolymers and/or block copolymers may be used as the copolymer. Preferred are polylactic acids.

Useful polylactic acids include lactic acid homopolymers. Also usable are copolymers prepared by copolymerization of lactic acid with a polyethylene glycol having a molecular weight of 600 or more in a molar proportion of 0.1 to 10%, an aliphatic polyester in a molar proportion of 0.1 to 80% or polycaprolactone in a molar proportion of 0.1 to 80%. Preferable are copolymers prepared by copolymerization of lactic acid with a polyethylene glycol having a molecular weight of 2,000 to 20,000 in a molar proportion of 0.1 to 10%, an aliphatic polyester in a molar proportion of 0.1 to 50% or polycaprolactone in a molar proportion of 0.1 to 50%.

Lactic acid is a stereoisomeric monomer and exists as L-lactic acid and D-lactic acid. Either isomer or a mixture of these isomers may be used as lactic acid in the invention. It is preferable to have an optical purity of at least 60%, more preferably 80% or higher. When the optical purity is low, the polymer tends to have low crystallinity, resulting in low heat resistance and inferior mechanical properties. When high elasticity is desired, the proper proportion of L-lactic acid is 70% or more, preferably 90% or more.

The biodegradable resins used in the present invention may be prepared by conventional methods. For example, polylactic acids can be prepared by known methods such as direct dehydration and polycondensation of lactic acid; or a method comprising dehydration of lactic acid into lactide and then subjecting the lactide to ring opening polymerization. It is convenient to use commercially available biodegradable resins. Examples of prototype and currently commercially available biodegradable plastics include, in addition to the already mentioned plastics, those known by the trade name "Biogreen" (polyhydroxybutyrate, product of Mitsubishi Gas Chemical Company, Inc.), the trade name "Corncol" (modified starch, product of Japan Corn Starch Co., Ltd.), the trade name "Celgreen PCA" (cellulose acetate, product of Daicel Chemical Industries, Ltd.), the trade name "Dolon CC" (chitosan/cellulose/starch, product of Aicello Chemical Co., Ltd.), and the trade name "Celgreen" (cellulose acetate-based material, product of Daicel Chemical Industries, Ltd.).

From the viewpoint of mechanical strength, it is preferable for the biodegradable resin of the invention to have a number average molecular weight of about 20,000 or more, preferably 40,000 or more, more preferably 60,000 or more, even more preferably 100,000 or more. From the viewpoint of heat resistance, it is preferable that the biodegradable resin have a melting point of 70° C. or higher, more preferably 100° C. or higher, even more preferably about 160° C.

The proportions of the biodegradable resin and the mannan digestion product vary depending on the kinds of resin and product. Therefore, it is difficult to specifically define the proportions. Generally, the degradation rate and functions of the biodegradable resin composition such as bacterial adsorption can be adjusted by changing the proportion of mannan digestion product to biodegradable resin. The biodegradability and bacterial adsorption properties can be enhanced by increasing the proportion of mannan digestion product. The resulting composition can suitably be used for objects requiring antimicrobial barrier properties and rapid degradability. When high strength is required, it is desirable to use galactomanno-oligosaccharide containing 80% or less of mannose as a mannan digestion product. The preferable proportional ranges of the components greatly differ depending on the intended use of the resin composition. The proportions can suitably be decided in view of the balance between physical properties such as strength and functions such as bacterial adsorption and biodegradability.

From the viewpoint of mechanical strength, it is adequate that the proportion of the mannan digestion product be usually 0.05 to 40 wt. %, preferably 0.5 to 10 wt. %, more preferably 1 to 5 wt. %, relative to 100 wt. % of the biodegradable resin.

From the viewpoints of degradation rate (biodegradability) and bacterial adsorption, it is adequate that the proportion of the mannan digestion product be usually 1 to 40 wt. %, preferably 5 to 20 wt. %, more preferably 5 to 10 wt. %, relative to 100 wt. % of the biodegradable resin.

With the purpose of functional improvement or addition of a new function, additives may be incorporated into the biodegradable resin composition in any proportions. Such additives include, for example, pigments, antioxidants, anti-static agents, matting agents, antiaging agents, fluorescent brighteners, UV absorbers, UV stabilizers, lubricants, fillers, carbon black, thickeners, chain extenders, crosslinking agents, crystal nucleating agents, plasticizers, stabilizers and viscosity stabilizers. The addition of a crystal nucleating

agent such as talc, boron nitride, calcium carbonate, magnesium carbonate or titanium oxide is especially preferred because it promotes crystallization during the thermoforming process and improves the heat resistance and mechanical strength of the molding. As long as the effects of the invention are not adversely affected, starch and processed starch, pectin, chitin, chitosan, alginic acid or a salt thereof, xyllose, cellulose or a cellulose derivative such as carboxymethylcellulose may also be added.

The biodegradable resin composition of the invention can be prepared by mixing the above biodegradable resin and the mannan digestion product with heating.

The method for mixing the biodegradable resin and the mannan digestion product is not specifically limited. Useful methods include a method comprising adding a mannan digestion product to a biodegradable resin while heating the resin, and mixing using a kneader such as a roll mill; a method comprising melting and kneading a mannan digestion product and a biodegradable resin in an extruder; blow molding; and foam molding. The heating temperature is usually in the range of 120° C. to 250° C. From the viewpoint of biodegradability, the range of 120° C. to 160° C. is preferable.

The biodegradable resin composition obtained can be processed, for example, by a method comprising heating and injecting the composition into an extrusion mold or can be dissolved in a solvent and formed into membranes, sheets, films or nets.

The biodegradable resin composition of the invention can thus be formed into various shapes such as films, sheets, plates, foams and bottles. Therefore, the composition can suitably be used for the following variety of purposes: packaging materials such as trays, foam trays, stretch films, shrink films, beverage bottles, and blister packaging for toothbrushes; agricultural and gardening materials such as greenhouse films, tunnel films, multi-purpose films, vegetation films, seedling pots, seed strings, and covering materials for fertilizers and pesticides; civil engineering materials such as vegetation nets, heavy bags, construction molds, civil engineering sheets and grass stakes; fishery materials such as fishing nets, laver nets, cultivation nets, fishing lines and fishing bait bags; waterproof sheets and packaging materials such as paper diapers and sanitary products; medical appliances such as syringes; commodities and sundry articles such as garbage bags, shopping bags, plastic bags, drain nets, laminated containers for dishes, spoons and forks, binding tapes, toothbrush and razor handles, shampoo and conditioner bottles, cosmetic bottles, pens and markers; medical materials such as osteosynthesis materials, suture materials and wound covering materials; air cleaning filters; magnetic cards, labels, mold release papers, golf tees, etc.

The biodegradable resin composition of the invention, as it is or after being formed into the desired shape, can be used as a blend by adding the composition to a suitable biodegradable resin. This use can reduce the costs of conventional biodegradable resins and biodegradable resin products (moldings) prepared using such resins and also improve biodegradability. Furthermore, new functions (antimicrobial barrier properties) can be imparted to conventional biodegradable resins.

EXAMPLES

Examples are given below to illustrate the invention in more detail, but it is to be understood that the invention is not limited thereby.

Example 1

Galactomannooligosaccharide (product of C.P.R. Co., Ltd.) was used as a mannan digestion product. Polylactic

acid ("Lacty #9000" manufactured by Shimadzu Corporation) was used as a biodegradable resin. The polylactic acid, talc and galactomannooligosaccharide were mixed at a weight ratio of 50:40:10 and kneaded in a Brabender Plastograph at 120° C. for 30 minutes. Polylactic acid ("Lacty #1012" manufactured by Shimadzu Corporation) was further added to the mixture at a weight ratio of 1:1 and kneaded in a high-speed mixer for 30 minutes. The resulting mixture was melted by heating and formed into pellets using a test extruder. The pellets were molded into a sheet with a thickness of about 500 μ m ["Lacty #1012": ("Lacty #9000" 50%/talc 40%/galactomannooligosaccharide 10%) =50:50]. This sheet was cut to a size of 100 mm \times 100 mm and tested.

Comparative Example 1

A resin composition was prepared in the same manner as in Example 1 except that talc was used in place of galactomannooligosaccharide, and molded into a sheet ["Lacty #1012": ("Lacty #9000" 50%/talc 50%) =50:50].

Comparative Example 2

A resin composition was prepared in the same manner as in Example 1 except that corn starch was used in place of talc and galactomannooligosaccharide, and molded into a sheet ["Lacty #1012": ("Lacty #9000" 50%/corn starch 50%) =50:50].

Experiment Examples

The sheets of the biodegradable resin compositions prepared in Example 1 and Comparative Examples 1 and 2 were measured with respect to the following parameters to evaluate their physical properties and functionalities:

1. Mechanical Properties

Fracture strength and fracture elongation were measured in accordance with JIS K-7113 at 17° C. at a humidity of 50%. Table 1 shows the results. Fracture strength and fracture elongation were calculated from the following formulas:

$$\text{Fracture strength (N/cm}^2\text{)} = \text{Fracture load (N)} / \text{Cross section (cm}^2\text{)}$$

$$\text{Fracture elongation (\%)} = \{(\text{Fracture elongation} - \text{Span length}) / \text{Span length}\} \times 100$$

TABLE 1

	Example 1*	Comp. Ex. 1*	Comp. Ex. 2
Thickness (mm)	0.503	0.491	0.504
Fracture strength (N/cm ²)	4448.9	4753.5	3364.0
Fracture elongation (%)	1.4	1.8	1.5

*In Table 1, Example 1 and Comparative Example 2 represent the average of 9 samples, and Comparative Example 1 represents the average of 5 samples.

These results confirm that the addition of a mannan digestion product to a biodegradable resin hardly affects the mechanical properties of the biodegradable resin such as fracture strength and fracture elongation.

2. Evaluation of Biodegradability

Flat plate films (10 cm \times 10 cm \times 0.2 cm thick) were prepared in accordance with the processes described in Example 1 and Comparative Example 1. Five sheets each of these films were buried 1) in activated sludge and 2) in soil. The biodegradability was evaluated from changes in weight. Reduction in weight (weight loss %) indicates the degree of biodegradation of the flat plate film. Table 2 shows the

results. In Table 2, Example 1 represents the average of 9 samples, and Comparative Example 1 represents the average of 5 samples.

TABLE 2

Weight loss %		
	Example 1	Comparative Example 1
1) Biodegradability in activated sludge (sewage treatment plant)		
Start (0 hour)	0	0
1 month later	86.1	30.1
2 months later	91.6	63.2
3 months later	98.1	78.5
2) Biodegradability in soil		
Start (0 hour)	0	0
1 month later	68.6	16.4
2 months later	88.4	40.9
3 months later	92.1	54.3

These results confirm that the addition of a mannan digestion product to a biodegradable resin significantly improves the biodegradability of the resin.

3. Evaluation of Bacterial Adsorption Capability

Flat plate films (10 cmx10 cmx0.2 cm thick) were prepared in accordance with the processes described in Example 1 and Comparative Example 1. Five sheets each of these films were placed into 500 ml flasks containing 100 ml of a bacteria culture medium (*Escherichia coli*, bacteria count: 2×10^8 bacteria/ml) and shaken. Then, the films were taken out and the bacterial count in the medium was determined. The adsorption % was determined from the reduction in bacterial count. Table 3 shows the results. In Table 3, Example 1 represents the average of 9 samples, and Comparative Example 1 represents the average of 5 samples.

TABLE 3

Bacterial adsorption %		
	Example 1	Comparative Example 1
Start (0 hour)	0	0
10 minutes later	27.8	0.2
30 minutes later	84.5	0.9
60 minutes later	90.9	4.3

The results confirm that the biodegradable resin composition of the invention containing a mannan digestion product in addition to a biodegradable resin has greatly improved bacterial adsorption capability.

INDUSTRIAL APPLICABILITY

The biodegradable resin composition and moldings thereof according to the present invention rapidly decompose completely in nature such as in soil or in water by the action of enzymes or bacteria without generating toxic substances. Therefore, after use, the biodegradable resin composition and moldings thereof can be disposed of, as they are or after grinding, by underground burial or under-water disposal.

Especially, the biodegradable resin composition of the invention prepared using a polylactic acid polymer as a biodegradable resin is transparent and useful as a biodegradable plastic (biodegradable product) with excellent toughness, flexibility and impact resistance. Therefore, this resin composition can suitably be used for various purposes especially requiring strength, such as beverage bottles,

shampoo and conditioner bottles, cosmetic bottles and like polyethylene terephthalate (PET) bottles; civil engineering materials such as construction molds and piles; fishery materials such as fishing nets and fishing lines; agricultural materials for vegetation and plastic greenhouses; vegetation materials; laminated containers for spoons and forks; toothbrush and razor handles; medical materials such as osteosynthesis materials and suture materials; sports goods such as golf tees; writing supplies such as pencil cases and plastic sheets laid under writing paper; clothing and industrial textile products; sanitation and medical related materials such as diapers, sanitary products, gauzes and patches.

By adjusting the proportion of the mannan digestion product, the biodegradable resin composition of the invention is further provided with bacterial adsorption capability. For example, if using textile products (clothing) made from such a biodegradable resin composition, bacteria once adsorbed on the products are difficult to desorb, whereby the dispersion of bacteria can be prevented. Such products are useful, for example, as antimicrobial barrier textile products effective for the prevention of nosocomial infection.

By adding a mannan digestion product to a biodegradable resin, the present invention can provide a biodegradable plastic (a biodegradable product) at a lower cost than single use of the biodegradable resin, while substantially maintaining the mechanical properties at the level achieved by a biodegradable plastic (a biodegradable product) composed of the biodegradable resin alone.

What is claimed is:

1. A biodegradable resin composition comprising a biodegradable resin and a mannan digestion product with the proviso that the biodegradable resin is not line cellulose.

2. The biodegradable resin composition according to claim 1 wherein the biodegradable resin is an aliphatic polyester.

3. The biodegradable resin composition according to claim 1 wherein the biodegradable resin is at least one member selected from the group consisting of polyhydroxybutyrate, polylactic acid, polycaprolactone, polybutylene succinate, polybutylene succinate/adipate, polybutylene succinate carbonate, polyvinyl alcohol and cellulose acetate.

4. The biodegradable resin composition according to claim 1 wherein the biodegradable resin is a polylactic acid polymer.

5. The biodegradable resin composition according to claim 4 wherein the polylactic acid polymer is a homopolymer or copolymer of lactic acid, or at least one copolymer of lactic acid and at least one member selected from the group consisting of cyclic lactone, glycolic acid, α -hydroxybutyric acid, α -hydroxyisobutyric acid, α -hydroxyvaleric acid, hydroxypentanoic acid, hydroxyhexanoic acid, hydroxyheptanoic acid, hydroxyoctanoic acid, ethylene glycol, polyethylene glycol, 1,4-butanediol, succinic acid and sebacic acid.

6. The biodegradable resin composition according to claim 1 wherein the biodegradable resin is a polylactic acid.

7. The biodegradable resin composition according to claim 1 wherein the biodegradable resin has a number average molecular weight of 20,000 or more and a melting point of 70° C. or higher.

8. The biodegradable resin composition according to claim 1 wherein the mannan digestion product is at least one member selected from the group consisting of mannooligosaccharides, galactomannan digestion products and glucomannan digestion products.

9. The biodegradable resin composition according to claim 1 wherein the proportion of the mannan digestion

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product is 0.05 to 40 wt. % relative to 100 wt. % of the biodegradable resin.

10. The biodegradable resin composition according to claim 1 wherein the proportion of the mannan digestion product is 1 to 40 wt. % relative to 100 wt. % of the biodegradable resin.

11. The biodegradable resin composition according to claim 1 which further comprises a crystal nucleating agent.

12. The biodegradable resin composition according to claim 11 wherein the crystal nucleating agent is at least one

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member selected from the group consisting of talc, boron nitride, calcium carbonate, magnesium carbonate and titanium oxide.

13. A biodegradable product produced by molding the biodegradable resin composition of claim 1.

14. A product with antimicrobial barrier properties produced from the biodegradable resin composition of claim 1.

* * * * *

**APPENDIX F: CITED OPINIONS OF THE BOARD OF PATENT
APPEALS AND INTERFERENCES**

None